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THE REDUCTION OF SILICOTUNGSTATES BY HYDROGEN

II THE REDUCTION OF CIS-SILICOTUNGSTIC ACID AND ITS POTASSIUM SALTS

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Introduction: Contradictory views are expressed in the foreign literature on the structure of the inner spheres of heteropoly acids. Miolati [1] and Rosenheim [2] believe that the Me_2O_7 radicals (where Me = W or Mo) are arranged about the central atom. Pfeiffer [3] thinks that the central atom in heteropoly acids is surrounded by six oxygen atoms, each of which coordinates two MeO_3 radicals; Keggin [4] asserts that the central atom has four Me_3O_{10} radicals attached to it, and so forth. None of these notions has been checked experimentally. It is the objective of this research of ours to make a critical evaluation of the existent views of the structure of the inner sphere of heteropoly acids and to make a thorough study of the problem. With this goal in view, we made a systematic investigation of the reduction of silicotungstates with hydrogen.

1. Reduction of cis-silicotungstic acid. The information in the literature on the reduction of silicotungstates (henceforth denoted by s.t.) by hydrogen is limited to a few patents [5], which merely indicate the feasibility of reducing silicotungstic (s.t.) acid and its salts. In our study of the reduction of s.t. acid and of all the subsequent potassium s.t., we employed the method described at length in our Report I [6]. When reducing cis-s.t. (henceforth denoted by c.s.t.) acid, we observed the dehydration of the compound and the loss of oxygen at the given reduction temperatures.

Marignac [7] has described a crystal hydrate of s.t. acid, with 28.3 molecules of water and a melting point of 36-35°. After being dried at 100°, s.t. acid retains a constant weight until 150°; it continuously loses about 5.23 molecules of water between 150 and 280°; the last molecules of water are lost somewhat above 250°, and the compound decomposes. Rosenheim [8] has described the same crystal hydrate as Marignac, with 28 molecules of water and a melting point somewhere between 25 and 40°; he also described a crystal hydrate with 22 molecules of water and a melting point of 53°

According to Copeau [9], s.t. acid contains 12 molecules of water at 105°. Crystals hydrates with 30, 29, 17, and 16 molecules of water are also described in the literature [10].

We have investigated the loss of water and of oxygen in s.t. acid by reducing it further with hydrogen at temperatures ranging from 200 to 800°. This resulted in the complete dehydration of the compound, followed by its reduction to metallic tungsten.

Doubly recrystallized s.t. acid was used for reduction; its analysis is given in Table 1.

TABLE 1

Percent found	% Calculated for an octabasic acid	% Calculated from the formula $[H_8[Si(W_2O_7)_6]$
WO_3 88.28	95.46	95.47
SiO_2 1.80	1.85	2.06
H_2O 10.68	2.5	2.46
Water, mols.....	17.5	—

Table 2 and Fig. 1 give the results of our reduction of the sample at temperatures ranging from 200 to 800°.

The data in Table 2 show that our findings are close to those of Marignac in the temperature range investigated, but it should be noted that calcining in hydrogen slows down the loss of water to such an extent that even at 400° the oxygen content of the substance is far from that of WO_3. Raising the temperature still higher causes the reduction of the tungstic anhydride, which passes through the lower stages of oxidation of tungsten (W_2O_5, WO_2, etc.) and is converted into the metal.

TABLE

Reduction of Cis-S.T.Acid

Test No.	Reduction temperature.	% Oxygen in the calcined sample	Color of Product	Composition of product and description of reduction process	Remarks
1	200°	28.2	White crumbly powder	Chemical combined water begins to be driven off	Percentage of oxygen in the initial c.s.t. acid in the reduction products (calc. from the formulas.
2	300	26.68	Whitish-gray powder	2 molecules of water are driven off	
3	400	24.36	Bluish-green	Last molecules of water driven off, coordination compound breaks down	
4	500	15.06	Brown-blue	W_2O_5 with a trace of WO_2	c.s.t. acid 28.28% WO_3 20.69% W_2O_5 17.86% WO_2 14.82%
5	600	8.42	Brown	WO_2 with a trace of W	
6	700	5.11	Dark gray	W with a trace of WO_2	
7	800	0.32	Gray metal	Practically pure tungsten	

2. Reducing the cis-silicotungstates of potassium with hydrogen. The greatest interest attaches to the reduction of pure s.t., from the standpoint of the link between tungsten bronzes and heteropoly compounds. This section deals with the results of the reduction of all the potassium cis-silicotungstates, from the mono- to the octasubstituted salts. The reduction conditions and the mode of operation were similar to those used in reducing potassium paratungstate and cis-s.t. acid. The composition of the reduction products was determined by subjecting

the samples of potassium s.t. to further analysis:

a) Visual examination of the reduced sample under the microscope, the color of the crystals yielding a fairly accurate evaluation of the presence of bronzes in the sample.

The crystals of the potassium bronzes are golden violet. Sometimes these crystals are scattered all over the field of view, but most often they exist as inclusions in a gray mass of other reduction products.

b) X-ray phase analysis was used to judge the presence of bronzes, by comparing the X-ray patterns of the pure bronzes with the X-ray photographs of the reduced s.t.

c) Chemical analysis for washed-out alkali. This method enabled us to determine chemically the temperature range in which the tungsten bronzes are formed and decomposed. The method is based upon the researches of V.I.Spitsyn, who found that a bronze decomposes at a reduction temperature of 700-800°, yielding a neutral tungstate, metallic tungsten, and water. As we know, a bronze does not dissolve in water, nor is it decomposed by it. Hence, the alkali combined as a bronze is not leached out by water, whereas the decomposition products of the bronze, K_2WO_4 or Na_2WO_4, are freely soluble and may be determined quantitatively. A detailed description of this method of analysis will be given in a separate report.

The results of our investigations of each silicotungstate are given in tables, figures, and X-ray photographs. M.A. Vladimirova was kind enough to do the X-ray analysis.

The computations of the individual X-ray patterns are given below.

3. Reduction of mono-, di-, and trisubstituted salts of cis-silicotungstic acid. The following salts were reduced:

$K_2O \cdot 2SiO_2 \cdot 24WO_3 \cdot 35H_2O$,
$K_2OSiO_2 \cdot 12WO_3 \cdot 13.5H_2O$, and
$3K_2O \cdot 2SiO_2 \cdot 24WO_3 \cdot 25.6H_2O$,

their chemical composition being given in Table 3.

The composition of these compounds indicates that this group of silicotungstates, containing little alkali (K_2O ranging from 1.61 to 4.47%), far from satisfies the alkali percentage specifications for the potassium bronze, $K_2W_4O_{12}$, where K_2O totals 9.34%). It was therefore unlikely that this group would yield bronzes; we confined our investigations of these samples to observing the behavior of the water and the general behavior of the silicotungstates when reduced with hydrogen in the 300-500° temperature range. In this case the method used to determine the loss of water during reduction was

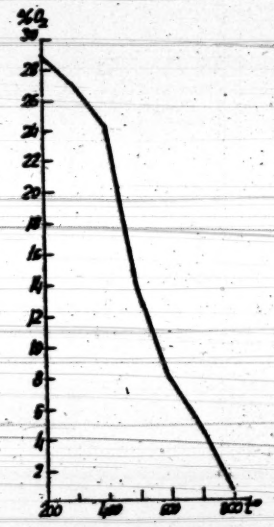

Fig. 1. Reduction of silicotungstic acid.

TABLE 3

Formula of salt	Per cent found					% recomputed for the anhydrous salt without impurities			% computed from the formula for the anhydrous salt		
	WO_3	K_2O	SiO_2	H_2O	Cl'	WO_3	K_2O	SiO_2	WO_3	K_2O	SiO_2
$2K_2O \cdot 2SiO_2 \cdot 24WO_3$.	85.66	1.61	1.86	10.95	None	96.05	1.80	2.05	96.30	1.63	2.07
$K_2O \cdot SiO_2 \cdot 12WO_3$....	87.18	3.09	1.83	8.23	None	94.65	3.33	1.99	94.76	3.28	2.04
$3K_2O \cdot 2SiO_2 \cdot 24WO_3$.	86.01	4.47	1.84	7.68	None	93.1	4.84	2.03	93.27	4.73	2.01

not the same as that used for the s.t. acid, the sample being calcined in air to constant weight, after which the per cent gain or loss in weight was determined.

The results of this analysis are set forth in Table 4, which shows that the silicotungstates also retain their water tenaciously, keeping 3 to 6 molecules of water even at 400°.

TABLE 4

Reduction of Mono-, Di-, and Trisubstituted Potassium Silicotungstates

Reducing temperature	Calcining losses						Remarks
	$K_2O \cdot 2SiO_2 \cdot 24WO_3$		$K_2O \cdot SiO_2 \cdot 12WO_3$		$3K_2O \cdot 2SiO_2 \cdot 24WO_3$		
	%	molecules	%	molecules	%	molecules	
300°	3.63	11	3.24	5.3	2.01	6	Some of the combined water eliminated
400	2.05	6.6	1.83	3	1.21	4	Combined water driven off and coordination compound decomposed
500	Gain in wt. 0.23	-	Gain in wt. 0.64	-	Gain in wt. 0.75	-	Reduction sets in

Reduction sets in at 500°, the rate of reduction rising with an increase in the per cent of K_2O. This is apparently due to the catalytic action of the K_2O, as has been pointed out by Koppelman [11].

Reduction of tetrasubstituted potassium cis-s.t. The formation of potassium bronzes may be expected when we reduce silicotungstates that contain more K_2O, beginning with the tetrasubstituted salt, which contains 6.3% K_2O; we therefor analyzed these reduced samples by all three of the methods set forth above. We used a potassium cis-s.t. with the formula $2K_2O \cdot SiO_2 \cdot 12WO_3 \cdot 17H_2O$, the chemical analysis of which is given in Table 5.

This salt was reduced at various temperatures. The reduction results are given in Table 6, which shows that the reduction of the tetrasubstituted potassium s.t. in the 200-500° range entails the elimination of the combined water. Decomposition and rearrangement, with the formation of bronzes, are observed at 500°; the bronzes are clearly visible under the microscope, though they are not

TABLE 5

Chemical Composition of Tetrasubstituted Potassium S.T.

Chemical compound	Per cent found	%, recomputed from the anhydrous salt	%, computed from the formula $2K_2O \cdot SiO_2 \cdot 12WO_3$
WO_3	82.23	91.78	91.8
SiO_2	1.74	1.94	1.97
K_2O	5.65	6.30	6.23
H_2O	10.26	-	-
Cl'	0.025	-	-

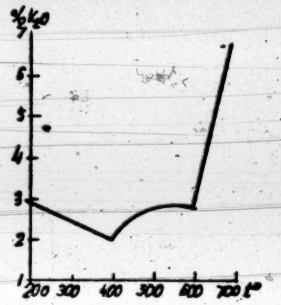

Fig. 2. Reduction of tetrasubstituted potassium silicotungstate.

yet seen in the X-ray pattern. The bronze lines appear in the X-ray photograph at 600°, though their number is exceedingly small.

Fig. 2 shows that the decomposition of a bronze is accompanied by a sharp rise in the quantity of alkali leached out, the curve changing direction abruptly whenever a bronze is formed.

TABLE 6

Reduction of Tetrasubstituted Potassium Cis-S.T.

Reducing temperature.	Total % K_2O	Per cent K_2O leached out, Test series I	Test series II	Microscope observations	X-Ray analysis
200°	6.30	2.91	2.72	White homogeneous powder	-
300°	6.30	2.46	2.68	Whitish-gray homogenous powder	-
400	6.30	1.88	1.99	Blue-gray powder	-
500	6.30	2.74	2.54	Blue-brown powder; violet crystals of the bronze are found	Non-equilibrium state; lines much blurred
600	6.30	2.85	2.71	Dark-brown powder; violet crystals of the bronze are found	Individual lines, close to the potassium bronze lines
700	6.30	6.61	6.19	Dark-gray powder; heterogeneous	-

The computation of the X-ray pattern is given in Table 7.

The first column of the table gives the serial numbers of the lines. Column 2 gives the observed visual density of the lines on the five-point system (very strong, strong, medium, weak, very weak). Column 3 gives the observed values of $\sin^2 \vartheta$. Column 4 gives the values of $\sin^2 \vartheta$ calculated for the standard potassium bronze.

For some of the X-ray photographs reproduced below (see Plate, page1300), we have added a fifth column indicating the Miller indices, h, k, l, for metallic

tungsten. Column 6 then gives the $\sin^2\vartheta$ calculated for metallic tungsten. The precision of measurement of the interlinear distances was 0.3 mm. The diameter of the chamber was 57.6 mm; the conditions under which the X-ray analysis was made did not differ from those described in our first report. The amount of alkali leached out indicates that bronzes were produced in Tests 6 and 8, at 400-500°, but the X-ray analysis shows that the characteristic crystals of a potassium bronze appear only in Tests 8 and 9, at 500-600°. Samples of s.t. of different composition were reduced in similar fashion. The results are set forth in the respective Tables.

Fig. 3. Reduction of pentasubstituted potassium silico tungstate.

TABLE 7

Computation of the X-Ray Pattern of a Sample of the Tetrasubstituted Salt, Calcined at 600°

Line No.	Density	$\sin^2\vartheta$, observed	$\sin^2\vartheta$, computed for a standard potassium bronze
1	Strong	0.72	–
2	Medium	0.092	–
3	Strong	0.122	–
4	Strong	0.142	–
5	Strong	0.169	–
6	Strong	0.209	0.212
7	Weak	0.224	–
8	Weak	0.239	0.234
9	Strong	0.256	0.253
10	Strong	0.284	0.284
11	Medium	0.327	0.322
12	Medium	0.356	0 –
13	Very Strong	0.383	0.389
14	Strong	0.400	–
15	Medium	0.415	0.422
16	Weak	0.446	–
17	Strong	0.470	–
18	Strong	0.500	–
19	Medium	0.566	–

5. Reduction of pentasubstituted potassium cis-s.t., $5K_2O \cdot 2SiO_2 \cdot 24WO_3 \cdot 12.4H_2O$. The chemical analysis of this salt is given in Table 8.

The results of reduction are given in Table 9 and Fig. 3; the decomposition of the bronze is accompanied by an abrupt change in direction of the curve. The X-ray patterns are also given.

The results of computing the X-ray patterns secured with the various samples of pentasubstituted potassium silicotungstate reduced at 600, 700, and 800° are listed in Tables 10, 11, and 12, and shown in Fig. 3, and in the X-ray photographs.

The results of the X-ray analysis of the reduced samples of pentasubstituted potassium cis-s.t. indicate that most bronzes are formed at 600°, where all of the dense lines are those of a potassium bronze. At 700 and 800° the density of the potassium bronze lines is much lower, the lines being greatly blurred in some instances. This signifies that the bronzes begin to decompose at temperatures above 600°, with more thoroughgoing reduction of the tungsten oxides.

TABLE 8

Chemical Composition

Chemical compound	Per cent found	Per cent recomputed from the anhydrous salt	Per cent computed from the formula $5K_2O \cdot 2SiO_2 \cdot 24WO_3$
WO_3	87.44	90.61	90.40
SiO_2 ...	1.87	1.94	1.95
K_2O	7.12	7.38	7.68
H_2O	3.61	-	-
Cl'	0.004	-	-

TABLE 9

Reduction of Pentasubstituted Potassium Cis-S.T.

Reduction temperature	Chemical analysis: Total % K_2O	Chemical analysis: % K_2O leached out	X-Ray Analysis	Microscopic observations
1	2	3	4	5
500°	7.38	2.54	Weak density, all lines blurred	Gray-white powder; undecomposed crystals of the salt; violet crystals of the bronze are found
600	7.38	3.68	Intense reflection from the tungsten space lattice; weaker reflection from the bronzes	Dark-gray powder; violet crystals scattered through the field.
700	7.38	6.92	Tungsten lattice predominates; only 4 lines coincide with the bronze lines	Dark-gray powder; individual violet crystals are encountered
800	7.38	7.03	Tungsten lines predominate; bronze lines present	Lustrous gray powder of metallic tungsten sin[2]

6. Reduction of the hexasubstituted potassium cis-s.t., $3K_2O \cdot SiO_2 \cdot 12WO_3 \cdot 16.6H_2O$. The chemical composition of this salt is given in Table 13.

The results of reducing the hexasubstituted salt are given in Table 14 and Fig. 4; Fig. 4 shows the abrupt changes in slope of the curve due to decomposition of the bronzes. We also reproduce the X-ray patterns of the salt; the results of X-ray computations are given in Tables 15 and 16.

7. Reduction of the heptasubstituted potassium cis-s.t. $7K_2O \cdot 2SiO_2 \cdot 24WO_3 \cdot 21.8H_2O$. The chemical composition of this salt is given in Table 17.

We reproduce the X-ray patterns of this salt; the reduction results are listed in Table 18, and the results of X-ray computations in Table 19.

Lastly, we reduced a sample of an octasubstituted salt; its analysis is given in Table 20.

TABLE 10

Computation of the X-Ray Pattern of the Pentasubstituted Salt, Reduced at 600°.

Line No.	Density	$\sin^2\vartheta$, observed	$\sin^2\vartheta$, computed for the standard potassium bronze	h,k,l for W	$\sin^2\vartheta$, computed for W
1	Blurred	0.0818	0,082	-	-
2	Blurred	0.102	0.0912	011	0.102
3	Very strong	0.121	-	011	0.119
4	Strong	0.142	-	-	-
5	Medium	0.152	-	-	-
6	Very strong	0.200	0.201	002	0.204
7	Very strong	0.239	0.235	002	0.238
8	Strong	0.286	-	-	-
9	Strong	0.298	0.294	112	0.306
10	Strong	0.328	0.333	-	-
11	Very strong	0.359	0.366	112	0.356
12	Medium	0.441	0.438	-	-
13	Medium	0.472	-	022	0.475
14	Strong	0.490	-	-	-
15	Strong	0.588	0.580	013	0.594
16	Strong	0.670	-	-	-
17	Blurred	0.700	0.698	-	-
18	Blurred	0.785	-	222	0.713
19	Strong	0.740	0.738	-	-
20	Very strong	0.830	-	123	0.832
21	Blurred	0.862	0.860	-	-
22	Strong	0.880	-	-	-

TABLE 11

Computation of the X-Ray Pattern of The Pentasubstituted Salt, Reduced at 700°.

Line No.	Density	$\sin^2\vartheta$,, observed	$\sin^2\vartheta$, computed for the standard platinum bronze	h, k, l, for W	$\sin^2\vartheta$, computed for W
1	Blurred	0.101	-	011β	0.102
2	Very strong	0.120	-	011α	0.119
3	Medium	0.144	-	-	-
4	Strong	0.240	-	002	0.238
5	Very blurred	0.290	0.294	-	-
6	Medium	0.305	-	-	-
7	Medium	0.329	0.330	-	-
8	Very strong	0.357	0.360	112α	0.356
9	Blurred	0.476	-	022α	0.475
10	Medium	0.497	-	-	-
11	Medium	0.512	-	-	-
12	Strong	0.596	-	013α	0.594
13	Strong	0.678	-	-	-
14	Weak	0.698	0,698	-	-
15	Weak	0.714	-	222α	0.713
16	Medium	0.750	-	-	-
17	Very strong	0.832	-	123α	0.832
18	Strong	0.786	-	-	-

Cu emission: Voltage: 30 kv. Current: 8 Ma. Exposure: 6 hours.

TABLE 12

Computation of the X-Ray Pattern of the Pentasubstituted Salt, Reduced at 800°

Line No.	Density	$\sin^2\vartheta$, observed	$\sin^2\vartheta$, computed for the standard potassium bronze	h, k, l for W	$\sin^2\vartheta$, computed for W
1	Very strong	0.121	–	011	0.119
2	Weak	0.181	0.182	–	–
3	Strong	0.240	–	002	0.238
4	Medium	0.291	0.294	–	–
5	Very strong	0.359	0.360	112	0.356
6	Very weak	0.387	0.390	–	–
7	Very weak	0.413	–	022	0.409
8	Strong	0.470	–	022	0.475
9	Weak	0.513	–	013	0.511
10	Very strong	0.588	–	013	0.594
11	Medium	0.670	0.668	–	–
12	Medium-strong	0.717	–	222	0.713
13	Weak	0.744	0.738	–	–
14	Very strong	0.838	–	123	0.832
15	Medium	0.863	0.860	–	–

TABLE 13

Chemical compound	Per cent found	Per cent recomputed from the anhydrous salt	Per cent computed from the formula $3K_2O \cdot SiO_2 \cdot 12WO_3$
WO_3	79.36	88.12	89.06
K_2O	9.09	9.7	9.64
SiO_2	1.89	2.02	1.92
H_2O	9.57	–	–
Cl'		–	–

TABLE 14

Reduction of Hexasubstituted Potassium Cis-S.T.

Test No.	Reduction temperature	Chemical analysis: Total % K_2O	Chemical analysis: % K_2O leached out	Microscopic observations	X-ray analysis
15	400°	9.70	4.84	Dark-gray heterogeneous powder; crystals of the undecomposed salt present	–
14	500	9.70	2.96	Blue-violet powder, bronze crystals present.	–
13	600	9.70	3.06	Dark-brown powder; violet bronze cryst. throughout field	Nearly all interference lines coincide with lines of the bronze standard
16	800	9.70	8.85	Gray powder of metallic tungsten	Interference lines from tungsten space lattice and weak reflections from the bronzes

Cu Emission. Voltage 30 kv. Current 8 Ma. Exposure 6 hours.

TABLE 15

Computation of the X-Ray Pattern of the Hexasubstituted Salt, Calcined at 600° *

Line No.	Density	$\sin^2\vartheta$ observed	$\sin^2\vartheta$ computed for a standard potassium bronze
1	Strong	0.139	-
2	Strong	0.170	-
3	Medium strong	0.196	0.192
4	Medium	0.209	0.212
5	Strong	0.235	0.234
6	Medium	0.258	0.253
7	Blurred	0.283	0.284
8	Medium	0.355	-
9	Strong	0.388	0.389
10	Strong	0.425	0.422
11	Strong	0.566	-
12	Weak	0.756	0.757
13	Strong	0.776	-
14	Strong	0.808	0.809
15	Strong	0.865	0.855

TABLE 16

Computation of the X-Ray Pattern of the Hexasubstituted Salt, Calcined at 800° **

Line No.	Density	$\sin^2\vartheta$, observed	$\sin^2\vartheta$, computed for the standard potassium bronze	h, k, l, for W	$\sin^2\vartheta$, computed for W
1	Very strong	0.121	-	011α	0.119
2	Blurred	0.163	0.166	-	-
3	Slightly blurred	0.190	0.182	-	-
4	Ditto	0.204	0.201	002β	0.204
5	Strong	0.240	0.235	002α	0.238
6	Weak	0.258	-	-	-
7	Medium	0.295	0.294	-	-
8	Very strong	0.360	0.360	112α	0.356
9	Weak	0.385	0.390	-	-
10	Weak	0.413	0.420	022β	0.409
11	Very strong	0.478	-	022α	0.475
12	Very strong	0.595	-	013α	0.594
13	Medium	0.669	0.668	-	-
14	Medium	0.714	-	222α	0.713
15	Very strong	0.828	-	123α	0.832

TABLE 17

Chemical compound	Per cent found	Per cent recomputed from the anhydrous salt	Per cent computed from the formula $7K_2O \cdot 2SiO_2 \cdot 24WO_3$
WO_3	82.11	87.77	87.73
K_2O	9.89	10.30	10.39
SiO_2	1.79	1.91	1.85
H_2O	6.18	-	-
Cl'	None	-	-

* Ni emission. Voltage: 30 kv. Current: 8 Ma. Exposure: 6 hours.

** Cu emission.

TABLE 18

Reduction of the Octasubstituted Potassium Cis-S.T.

Reduction temperature	Chemical analysis: Total % K_2O	Chemical analysis: % K_2O leached out	X-Ray Analysis	Microscope observations
500	10.30	5.51	Low line density; all lines blurred; computation impossible	Homogeneous gray-white powder
600	10.30	-	-	Dark-gray powder; violet bronze crystals are frequent
700	10.30	94.6	Tungsten lattice predominates; five lines coincide with those of a bronze	Gray powder; no bronze seen
800	10.30	-	-	Light gray, slightly caked pieces

TABLE 19

Computation of the X-Ray Pattern of the Heptasubstituted Salt, Reduced at 700°

Line No.	Density	$\sin^2\vartheta$, observed	$\sin^2\vartheta$, computed for the standard potassium bronze	h, k, l, for W	$\sin^2\vartheta$, computed for W
1	Medium	0.101	-	011β	0.102
2	Very strong	0.120	-	011α	0.119
3	Weak	0.143	-	-	-
4	Slightly blurred	0.197	0.201	002β	0.204
5	Strong	0.240	0.235	002α	0.238
6	Weak	0.292	0.294	-	-
7	Weak	0.329	0.330	-	-
8	Very strong	0.357	0.360	112α	0.356
9	Strong	0.473	-	022α	0.475
10	Medium	0.495	-	-	-
11	Very strong	0.597	-	013α	0.594
12	Strong	0.677	-	-	-
13	Medium	0.716	-	222α	0.713
14	Medium	0.748	-	-	-
15	Very strong	0.828	-	123α	0.832

TABLE 20

Chemical compound	Per cent found	Per cent recomputed from the anhydrous salt	Per cent computed from the formula $4KO_2 \cdot SiO_2 \cdot 12WO_3$
WO_3	79.55	86.09	86.46
K_2O	10.93	11.83	11.74
SiO_2	1.82	1.97	1.86
H_2O	7.60	-	-
Cl'	None	-	-

X-Ray 1. Tetrasubstituted potassium silicotungstate; reduction temperature 800°.

X-Ray 2. Tetrasubstituted potassium silicotungstate; reduction temperature 850°.

X-Ray 3. Pentasubstituted potassium silicotungstate; reduction temperature 650°.

X-Ray 4. Pentasubstituted potassium silicotungstate; reduction temperature 700°.

X-Ray 5. Pentasubstituted potassium silicotungstate; reduction temperature 800°.

X-Ray 6. Pentasubstituted potassium silicotungstate; reduction temperature 850°.

X-Ray 7. Hexasubstituted potassium silicotungstate; reduction temperature 650°.

X-Ray 8. Heptasubstituted potassium silicotungstate; reduction temperature 650°.

X-Ray 9. Heptasubstituted potassium silicotungstate; reduction temperature 700°.

X-Ray 10. Octasubstituted potassium silicotungstate; reduction temperature 650°.

X-Ray 11. Octasubstituted potassium silicotungstate; reduction temperature 700°.

X-Ray 12. Octasubstituted potassium silicotungstate; reduction temperature 850°.

Table 21

Reduction of Octasubstituted Potassium Cis-S.T.

Reduction temperature	Chemical analysis: Total % K_2O	Chemical analysis: % K_2O leached out	X-Ray analysis	Microscope observations
500°	11.83	5.81	Low density; lines blurred	Gray-white heterogeneous powder
600	11.83	6.36	All the intense reflections are from the potassium bronze lattice; very weak tungsten lines	Brown-gray powder; violet bronze crystals scattered throughout the field
700	11.83	11.30	Intense reflections from the tungsten lattice and from an unknown constituent	Dark-gray powder
800	11.83	11.44	Tungsten lattice predominates; negligible number of weak lines, close to those of the bronzes	Light gray clinkered pieces of metal

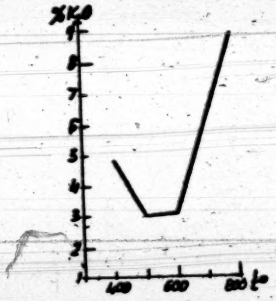

Fig. 4. Reduction of hexasubstituted potassium silicotungstate.

Fig. 5. Reduction of ocatsubstituted potassium silicotungstate.

8. Reduction of octasubstituted potassium cis-s.t. $4K_2O \cdot SiO_2 \cdot 12WO_3 \cdot 14H_2O$.

The results of the reduction of this salt are given in Table 21 and Fig. 5, where the instant at which a bronze decomposes is indicated by an abrupt change in the slope of the curve. We reproduce the X-ray patterns of this salt, while Tables 22, 23, and 24 give the computations of the X-ray patterns of the octasubstituted salt.

TABLE 22

Computation of the X-ray Pattern of the Octasubstituted Salt, Reduced at 600°

Line No.	Density	$\sin^2\vartheta$, observed	$\sin^2\vartheta$, computed for the standard potassium bronze	h, k, l for W	$\sin^2\vartheta$, computed for W
1	Strong	0.675	0.0688	-	-
2	Medium	0.0820	0.0825	-	-
3	Strong	0.0961	0.0912	011β	0.102
4	Very strong	0.114	-	011α	0.118
5	Strong	0.143	-	-	-
6	Medium-strong	0.164	0.166	-	-
7	Strong	0.199	0.201	002β	0.204
8	Strong	0.239	0.235	002α	0.238
9	Weak	0.261	-	-	-
10	Weak	0.287	0.294	-	-
11	Weak	0.310	-	112β	0.306
12	Very strong	0.329	0.332	-	-
13	Medium	0.350	-	112α	0.356
14	Strong	0.485	-	022α	0.475
15	Medium	0.495	-	-	-
16	Very strong	0.672	0.668	-	-
17	Strong	0.699	0.698	-	-
18	Very strong	0.442	0.738	-	-
19	Very strong	0.835	-	123α	0.832
20	Medium	0.860	0.860	-	-
21	Very strong	0.885	-	-	-

W - - - - - - - -
Cu emission.

CONCLUSIONS

A study of the reduction of potassium s.t. indicates that the mono-, di-, and trisubstituted salts retain a substantial amount (up to 17.6 molecules) of combined water at 300°, the salts beginning to decompose only at 400°.

Beginning with the tetrasubstituted potassium s.t., one of the reduction products is a violet potassium bronze. The bronzes appear in all the potassium silicotungstates tested at 500°; the X-ray patterns secured for some of the s.t. reduced at 500° are unclear, however, most of the lines being blurry, which indicates an irregular arrangement of the atoms in the crystal lattice, i.e., a rearrangement of the latter.

The densest lines characteristic of the potassium bronze standard are found in the potassium s.t. reduced at 600°, the number of such lines increasing with a rising percentage of potassium in the s.t., reaching a maximum in the octasubstituted salt. At 700°, all the s.t. salts clearly display the lines of metallic tungsten alongside those of the bronzes, the tungsten lines being much denser.

At 800°, the tungsten lines predominate in all the tested s.t. salts, the bronze lines being very weak. The formation of bronzes, which we were the first to observe in the reduction of s.t. salts, is of extremely great significance in resolving the problem of the structure of the inner sphere of heteropoly acids.

TABLE 23

Computation of the X-Ray Pattern of the Octasubstituted Salt, Reduced at 700°.

Line No.	Density	$\sin^2\vartheta$, observed	h, k, l	$\sin^2\vartheta$, computed for W	Remarks
1	Blurred	0.100	011β	0.102	
2	Very strong	0.120	011α	0.119	
3	Medium	0.143	-	-	
4	Weak	0.163	-	-	
5	Blurred	0.202	002β	0.204	
6	Medium-strong	0.239	002α	0.238	
7	Weak	0.309	112β	0.3069	
8	Medium-strong	0.332	-	-	No reflections corresponding to those of the potassium bronze standard
9	Very strong	0.360	112α	0.356	
10	Very weak	0.376	-	-	
11	Medium	0.479	022α	0.475	
12	Medium	0.496	-	-	
13	Weak	0.508	013β	0.512	
14	Very strong	0.597	013α	0.594	
15	Strong	0.678	-	-	
16	Blurred	0.700	-	-	
17	Medium	0.713	122α	0.713	
18	Medium	0.750	-	-	
19	Very strong	0.834	123α	0.832	
20	Strong	0.885	-	-	

TABLE 24

Computation of the X-Ray Pattern of the Octasubstituted Salt, Reduced at 800°.

Line No.	Density	$\sin^2\vartheta$, observed	$\sin^2\vartheta$, computed for the standard potassium bronze	h, k, l, for W	$\sin^2\vartheta$, computed for W
1	Medium	0.1015	-	011β	0.1023
2	Very strong	0.123	-	011α	0.119
3	Strong	0.238	-	002α	0.238
4	Medium	0.295	0.294	-	-
5	Very strong	0.358	0.360	112α	0.356
6	Strong	0.480	-	022α	0.475
7	Very strong	0.592	-	013α	0.594
8	Medium	0.672	0.668	-	-
9	Medium	0.710	-	222α	0.713
10	Very strong	0.832	-	123α	0.832
11	Medium	0.860	0.810	-	-

Tungsten bronzes are also produced during the reduction of potassium paratungstates; it is therefore highly likely that WO_3 radicals are coordinated about the oxygen atoms in the inner sphere of heteropoly acids (Pfeiffer); hence, the paratungstates and the fully saturated heteropolytungstates have the same structure in their inner spheres and thus yield the same reduction products - tungsten bronzes.

Cu emission.

SUMMARY

1. The reduction of cis-silicotungstic acid and of its eight potassium salts with hydrogen has been investigated for the first time.

2. The mono-, di-, and trisubstituted salts are dehydrated at first and then reduced to metallic tungsten.

3. It has been found that at 500°, beginning with the tetrasubstituted potassium cis-s.t., one of the reduction products is a violet potassium bronze.

4. The reduction products of potassium s.t. were investigated by X-ray analysis, microscopically, and analytically.

5. The reduction of cis-silicotungstic acid and its salts sets in at 500°; constitutional water is lost and the heteropoly anion is broken down between 200 and 500°.

6. The optimum temperature for the formation of bronzes is 600°; at 700° the bronze lines are not as dense, while the tungsten lines are clearly marked; and at 800° the tungsten lines predominate.

7. In the inner spheres of fully saturated heteropoly acids the central atom is apparently coordinated to six atoms of oxygen, which, in turn, are surrounded by twelve WO_3 (or MoO_3) radicals.

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DIAGRAMS FOR DETERMINING THE EFFICIENCY OF RECTIFYING COLUMNS BY MEANS OF THE BENZENE - CARBON TETRACHLORIDE SYSTEM. II

I. N. Bushmakin

In searching the literature on the methods of determining the efficiency of columns (the number of steps), one is struck by the fact that most authors make no special effort to secure precise information on efficiency. This may be due to the fact that efficiency is not regarded as an absolute quantity at the present time: it is believed that it depends on the concentration of the solution distilled, the nature of the solution's constituents, and the boiling rate (reflux return), besides being able to fluctuate widely as the result of channeling even when all the foregoing factors are held constant. That is why efficiency is regarded as a conventional quantity, its numerical value being an approximate figure and serving for comparative evaluation of the separating action of columns.

The number of steps is determined either by operating the column in a closed cycle (with 100% recycling of the reflux) or by operation in which part of the reflux is tapped off. In our research we were interested in the precise determination of efficiency during complete reflux return, so that in this paper we shall not deal with the second method of determining efficiency.

The literature contains very many proposed binary systems for the determination of column efficiency. Very often authors propose a new system without indicating in what way it is superior to previous ones. Apparently, what is involved is the ability of a laboratory to secure pure liquids for preparing the binary solution. That may be the case with systems that can be used to determine a comparatively small number of steps.

There are not many systems known for determining the number of steps of high efficiency columns. For a long time the methylcyclohexane-n-heptane system, proposed by Fenske [1], was used. Recently Willingham and Rossini [2] have suggested the following systems for this purpose: 2,3,3-trimethylpentane-2,3,4-trimethylpentane and 2,4-dimethylhexane-2,5-dimethylhexane.

The number of steps is determined as follows: One of the proposed solutions is poured into the still. The tower is operated on a closed cycle until equilibrium is reached. Samples of liquid are taken from the still and from the condenser, and their compositions determined (usually refractometrically), after which the number of steps is computed. There are several methods of computing the number of steps.

1. Graphical method. To begin with, the data on the liquid-vapor equilibria in the given system are used to plot an x,y diagram. Steps are laid off on this diagram and numbered, starting with some low concentration of the more volatile constituent and going up to some higher concentration. The concentration of the reflux in the condenser is determined, and the number of the corresponding step is found in the diagram (this may be a fractional number, say, 30.6); this

operation is repeated for the composition of the solution in the still. Subtracting the second number from the first, we get the total number of steps (the number of theoretical plates + the still-column transition).

This method is simple and convenient. It can be used only for the determination of the number of steps in low-efficiency columns, however. At high concentrations of the more volatile constituent, the curve representing the composition of the vapor in the x,y diagram is close to the diagonal that gives the composition of the liquid, and the steps become small. No matter how carefully they are plotted, an error is introduced; this error grows as the steps grow smaller and becomes additive. That is why this method may be used only to determine a number of steps that does not exceed a certain value. The maximum number of steps depends, of course, on the course of the curve representing the vapor composition, that is, on the system chosen.

There are various modifications of this method, but all of them can be used only to determine a small number of steps.

2. Analytical method. After equilibrium has been established in the column, the following equation relates the composition of the reflux in the condenser to that of the solution in the still:

$$\frac{y_n}{100 - y_n} = \alpha_1 \cdot \alpha_2 \cdot \alpha_3 \ldots\ldots \alpha_n \frac{x_1}{100 - x_1} \qquad (1)$$

where y_n is the molar percentage of the more volatile constituent in the condenser reflux; x_1 is the molar percentage of the more volatile constituent in the still; α_1 is the relative volatility in the transition from the liquid in the still to the vapor above it; α_2 is the relative volatility in the transition from the first theoretical plate to the vapor above it, etc.; and n is the number of evaporations in the column (the number of steps). α varies with the composition. Its variation is so slight for systems that approach an ideal solution that it may be assumed to be a constant. Then Equation (1) becomes:

$$\frac{y_n}{100 - y_n} = \alpha^n \frac{x_1}{100 - x_1} . \qquad (2)$$

One of the systems with an α that changes but little is methylcyclohexane-n-heptane. According to Willingham and Rossini [2], the α for this system ranges from 1.07584 to 1.07380 at concentrations that approach 0% and 100% of n-heptane, respectively. Fenske [1] assumed the α to be constant, 1.07, for this sytem; Willingham and Rossini propose that the value of α be taken as the midpoint of the $x_1 - y_n$ section of the curve. As will be shown below, the computation based on Fenske's assumption does not yield accurate results, while the Willingham and Rossini computation is quite accurate. This system may be employed to determine the efficiency of columns with somewhat more than 100 steps.

The disadvantages of this system are the unavailability of the constituents and the difficulty of accurately determining the concentration at low and high percentages of n-heptane in the solution (Tongberg [3]).

The systems suggested by Willingham and Rossini [2] were mentioned above. In these systems, α varies even less with composition. These systems can be used to determine the efficiency of columns with more than 200 steps. (The authors do not state the upper efficiency limit up to which these systems may be employed). The efficiency may be determined, apparently, with great accuracy.

The disadvantages of these systems is the fact that their constituents are even harder to obtain than those in the methylcyclohexane – n-heptane system, and the difficulty of analysis. The latter is done by meansof infrared spectrometers.

3. The combined method (analytical plus graphical). When α varies appreciable with concentration, Bragg [4] computes the number of steps as follows. He divides a large concentration range into 'small' intervals, finds the value of α (α is the concentration of the volatile in the liquid) for the midpoints of these intervals, calculates the number of steps for each interval from Equation (2), using the average α for the intervals, totals the number of steps, and plots a diagram (the number of steps versus the refractive index of the liquid). This diagrams looks like Fig. 1. He considers the fact that the calculated number of steps lie on the curve to be an index of the correctness of the computation.

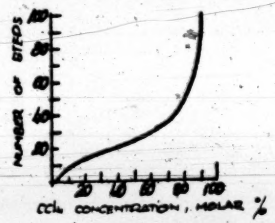

Fig. 1.

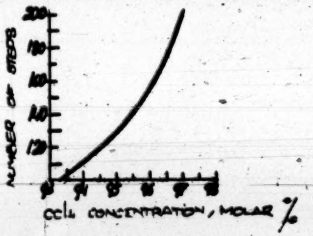

Fig. 2.

That is how Bragg plotted a diagram for the dichloroethane – benzene system. The calculation of steps in that diagram is hardly accurate. To begin with, the course of the α-concentration curve is a matter of doubt, owing to the great scattering of the experimental points. Then, the method of computation based on 'small' intervals may also be inaccurate, for reasons that will be set forth below.

In our laboratory we made a very careful study of the liquid-vapor equilibria in the benzene – carbon tetrachloride system, covering the range of 3-99.5 molar per cent of CCl_4 [8]. The constituents of this system are in adequate supply. They can be readily purified, and the concentration can be determined refractometrically with high accuracy. This system is ordinarily employed to determine the number of steps in low-efficiency columns (less than 50 steps), the computation being made graphically (Method I).

We decided to employ this system to determine the number of steps of high-efficiency columns. As computation and an experimental check both proved, this system can be employed to measure the efficiency of columns with as many as 500 steps.

In the benzene-carbon tetrachloride system, α varies with concentration in conformity with the equation $\alpha = 1.203 - 0.00203\ x$, where x is the molar % of CCl_4 in the liquid. When α varies, the number of steps should be computed as follows. Assigning the molar % of CCl_4 in the liquid (x_1) and knowing the corresponding value of α_1, we calculate the molar % of CCl_4 in the vapor (y_1) from the equation:

$$\frac{y_1}{100 - y_1} = \alpha_1 \frac{x_1}{100 - x_1} . \qquad (3)$$

This value of y_1 is the molar % of CCl_4 in the vapor above the liquid in

the still and x_2 is the molar % of CCl_4 in the first step. Knowing x_2 and the corresponding value of α_2, we compute y_2, etc., until we reach the concentration of CCl_4 in the condenser reflux. The sum of the changes in concentration $x_1 - y_1$, $x_2 - y_2$, etc., computed in this manner is obviously the number of steps. The results of this computation may be plotted in a diagram (number of steps versus concentration), after which this diagram may be used to determine the number of steps.

In the form described above this calculation is too laborious. It may be replaced by an approximate calculation resembling the one used by Bragg. The concentration range is divided into small intervals and the number of steps, n, is calculated for each interval from Equation (2), assuming that α does not change throughout the interval and equals the value it has at the midpoint of the interval.

The correctness of such a calculation depends upon the choice of size of the concentration intervals. Equation (2) is an approximation when α varies, and is incorrect for large intervals. As the interval is shortened, the error in the calculation of n (both absolute and relative) diminishes, finally becoming so small as to be negligible. The size of these intervals depends on the nature of the system's constituents and the concentration range in which the intervals fall, being determined by trial and error. An interval is selected, and n is calculated for this interval; then the interval is divided in two, and the corresponding values of n are computed for each half. If the sum of the latter differs from the n for the large interval by an amount that cannot be ignored, the interval selected is excessively large. A smaller interval is chosen, and the same calculation is repeated. Examples of such calculations are given in Table 1.

TABLE 1

Examples of Selecting the Size of the Concentration Intervals

Concentration interval	Number of steps, n	Σ n	Concentration interval	Number of steps n	Σ n
70-80 molar % CCl_4 ...	10.84	10.84	92-96 molar % CCl_4 ...	61.7	61.7
70-75 molar % CCl_4 ...	4.62	11.02	92-94 molar % CCl_4 ...	22.2	65.1
75-80 molar % CCl_4 ...	6.40		94-96 molar % CCl_4 ...	42.9	
70-72.5 molar % CCl_4..	2.19	11.10	92-93 molar % CCl_4 ...	9.7	65.9
72.5-75.0 molar % CCl_4	2.49		93-94 molar % CCl_4 ...	12.8	
75.0-77.5 molar % CCl_4	2.94		94-94.5 molar % CCl_4..	7.9	
77.5-80.0 molar % CCl_4	3.48		94.5-95.0 molar % CCl_4	9.5	
			95.0-95.5 molar % CCl_4	11.6	
			95.5-96.0 molar % CCl_4	14.4	

These figures indicate that the interval 70-80% is too big, but that the 70-75% and 75-80% intervals are acceptable, and the 70-72.5%, 72.5-75.0%, etc., intervals are even more acceptable. Likewise, the 92-96% interval is too wide, but the 92-94% and 94-96% intervals are almost acceptable, and the 92-93%, etc., intervals are wholly acceptable.

The paper by Bragg [4] contains no indication of how the sizes of the concentration intervals was selected. It is merely stated that the intervals were small. Table 1 indicates that the size of "small" intervals depends upon the concentration range in which they fall; for that reason the correctness of Bragg's calculation is open to doubt. I divided the concentration range of 3 to 99 molar %

of CCl_4 into intervals by the method given above and computed the number of steps accordingly.

The results of the computation are given in Table 2. We were able to plot 5 diagrams (number of steps versus concentration) like Figs. 1 and 2 from the data in this table.

TABLE 2

Data for Plotting Number of Steps – Concentration Diagrams *

Concentration of CCl_4 in the condenser reflux, molar %	Number of steps	Concentration of CCl_4 in the condenser reflux, molar %	Number of steps	Concentration of CCl_4 in the condenser reflux, molar %	Number of steps	Concentration of CCl_4 in the condenser reflux, molar %	Number of steps
Diagram I				Diagram III			
3.0	0.0	75.0	39.4	97.07	200	97.80	257
5.0	2.9	77.5	42.3	97.25	211	97.90	269
7.5	5.4	80.0	45.8	97.35	218	98.00	281
10.0	7.3	82.0	49.2	97.50	230	98.05	287
15.0	10.1	84.0	53.3	97.60	238	98.10	294
20.0	12.3	85.0	55.6	97.70	247	98.14	300
25.0	14.3	87.0	61.4	Diagram IV			
35.0	18.0	89.0	69.1				
50.0	23.6	90.0	74.2	98.14	300	98.40	344
60.0	28.2	91.0	80.3	98.20	309	98.45	354
65.0	31.1	92.0	87.8	98.25	317	98.50	365
70.0	34.7	93.0	97.6	98.30	325	98.55	376
72.5	36.9	93.2	100.0	98.35	334	98.60	389
						98.64	400
Diagram II							
93.20	100	96.50	172	Diagram V			
94.00	110	96.60	176				
94.50	118	96.70	180	98.64	400	98.900	485
95.00	127	96.80	185	98.70	416	98.925	496
95.50	139	96.90	190	98.75	431	98.950	507
96.00	153	97.00	196	98.80	448	98.975	519
96.25	162	97.07	200	98.85	466	99.000	531

To calculate the number of steps from these diagrams, one has to determine the CCl_4 concentration in the liquid in the still and in the condenser, find the corresponding numbers of steps in the diagrams, and subtract the number of steps corresponding to the concentration in the still liquid from the number of steps corresponding to the concentration in the reflux.

The concentration of CCl_4 in the still and condenser liquids may be determined with an Abbe refractometer for efficiencies up to 80 steps.

The data for plotting the diagram (refractive index versus concentration) are listed in Table 3.

Measuring efficiencies above 80 steps requires the use of a Pulfrich photometer or another make of equal accuracy of readings. For the concentrations of 90 to 99% CCl_4 we used a diagram (Pulfric photometer drum readings versus concentration). That is why I have plotted on the diagrams the number of steps versus

* Concentration of CCl_4 in the still: 3 molar %.

concentration, rather than the refractive index.

On the basis of the numerical data in my possession underlying the data in Table 2, I estimate the error in computing that table to be less than 1%. Errors in determining concentrations may introduce much greater errors.

Table 4, which was computed from Table 2, gives the errors in the number of steps due to errors in determining the concentrations.

TABLE 3

Variation of the Refractive Index of Benzene – Carbon Tetrachloride Solutions with Concentration

CCl_4 concentration, molar %	n_D^{20}	CCl_4 concentration molar %	n_D^{20}
0	1.5011	50	1.4808
3	1.4999	55	1.4787
5	1.4991	60	1.4767
10	1.4971	65	1.4747
15	1.4950	70	1.4727
20	1.4930	75	1.4706
25	1.4910	80	1.4685
30	1.4889	85	1.4665
35	1.4869	90	1.4644
40	1.4849	95	1.4623
45	1.4828	100	1.4603

TABLE 4

Errors in the Number of Steps due to Errors in Determining the Concentration, Using Abbe and Pulfrich Photometers

(CCl_4 concentration in the still liquid: 3 molar %)

Abbe refractometer, error ± 0.25 molar %		Pulfrich refractometer, error ± 0.025 molar %	
Number of steps	Error	Number of steps	Error
0	± 0.3 steps	100	± 0.3 steps
10	± 0.1	150	± 0.7
25	± 0.1	200	± 1.5
50	± 0.5	250	± 2.5
75	± 1.4	300	± 4.0
100	± 3.2	350	± 5.0
		400	± 7.0
		450	± 9.0
		500	±11.0

Upon examination of the last entries in Table 2, doubt may arise as to the possibility of establishing equilibrium in a column with an accuracy of hundredths of a per cent in the concentration of the condenser liquid, i.e., doubts concerning the feasibility of measuring efficiencies in excess of 250 steps. To settle this question, I took a 100-step column andmeasured its efficiency when operating with solutions corresponding to those in Diagrams II, III, IV, and V.

The results of these measurements are listed in Table 5.

Table 5 indicates that: 1) the determination of the liquid-vapor equilibria were made correctly; 2) the computation of Table 2 was correct; 3) determination of efficiency up to 500 steps is quite feasible.

We now employ the method used to draw up Table 5 to check the correctness of data on liquid-vapor equilibria. In our previous paper [5] we set forth a method of checking these data in the α – concentration diagram. Whenever some portion of the α – concentration diagram inspires doubt, we check it in the column, the check being made as follows. The number of steps is calculated for the interval to be checked (as in the computation of Table 2), a similar calculation being made for a completely dependable interval. Then the efficiency of the column is determined with solutions corresponding to these intervals. If the efficiencies coincide, the doubtful interval is correct.

A check of this sort may reveal a systematic error in the determinations of the liquid-vapor equilibria that is not always disclosed by a check of the α –

α - concentration diagram or a check of the Duhem-Margules equation. A recurring error in determining the liquid-vapor equilibria yields different errors in computing the number of steps at different concentration intervals.

TABLE 5

Experimental Check of the Correctness of the Figures in Table 2

Molar % of CCl_4 in the still liquid	Molar % of CCl_4 in the condenser reflux	Number of steps	Remarks
7.0, equivalent to 5 (±0.2)* steps according to Table 2	93.61, equivalent to 105 (±0.3)* steps according to Table 2	100 (±0.5)*	Mean of several measurements
93.46, 103 ±(0.3) steps	97.06, 200 (±1.5) steps	97 (±2)	One measurement
97.06, 200 (±1.5) steps	98.16, 303 (±4) steps	103 (±6)	One measurement
98.12, 297 (±4.0) steps	98.64, 400 (±7.0) steps	103 (±11)	One measurement
98.62, 394 (±7.0) steps	98.94, 501 (±11) steps	107 (±18)	One measurement

Experiments in our laboratory have shown that accurate efficiency data can be secured up to 80steps by using benzene and carbon tetrachloride that are not highly pure.

The n_D^{20} of the benzene may be 1.5009-1.5011, and that of the carbon tetrachloride 1.4603-1.4604. The solution made up of these not too pure constituents is freed of the more highly volatile impurities in the efficiency determination itself, during the establishment of equilibrium in the column.** The column is operated in a closed cycle for the length of time required to establish equilibrium (this requires about 4 hours at an efficiency of 80 steps). Then some of the reflux is taken from the condenser (about 1 ml for a reflux rate of 200 drops per minute), and its refractive index is measured. These samples - 'discards' - are taken every 30 minutes. At first the refractive indexes of the discards vary substantially, since they contain diminishing percentages of the more volatile impurities. After these impurities have been eliminated, the refractive indexes of the discards begin to approach one another. The column is then allowed to operate for another hour, until complete equilibrium is reached, and samples are taken. The samples are much smaller than the discards. They must be small to keep them from disturbing the equilibrium in the column. The sample must be a quantity of liquid that is slightly in excess of the amount needed for a single measurement of the refractive index in an Abbe refractometer. These samples are likewise taken every 30 minutes. After the refractive indexes of a series of successive samples are exactly alike, a sample is taken from the still. This sample is taken from the still's side tube. The tapping may be done with a special device (consisting of a pipet attached to the tube by a ground glass

*This indicates the possible deviations, in conformity with Table 4.

**A slight inaccuracy in the refractive index of the still liquid has very little effect upon the results of the efficiency determination (Table 4).

fitting and equipped with a three-way stopcock connected to the still, the pipet reservoir, and the sample collector) or simply by removing the ground-glass stopper of the tube and quickly inserting instead a pipet with a stopper. This must be done quickly to prevent the reflux leaking out of the column and changing the concentration in the still.

If high accuracy is not required, an efficiency of 80-100 steps may be measured in this manner.

Determining efficiencies of 100 steps and more requires benzene and carbon tetrachloride that possess good physical and chemical constants,* and each of them must be separately freed of its more volatile impurities.

This refining of the constituents may be performed in the same column whose efficiency is to be determined, or, better still, in a column whose efficiency is known to be high. This refining is done by distilling into the column, alternating with closed-cycle operation of the column, until a sample taken from the condenser at equilibrium exhibits a refractive index that is the same as that of the liquid taken from the still (as measured on the drum of a Pulfrich refractometer). The solution for determining the efficiency is made up of the constituents purified in this manner.

To secure the data entered in Table 5 I measured the efficiency as follows. The efficiency of the column was first stabilized by filling it chockfull five times with a cold jacket.

The experiment was begun with a choked column and cold jacket. After this choking the column was shifted to trickling operation (200 drops per minute), and the jacket was heated to 76°. Four hours after trickling operation had been started the first discard of 2 ml was taken, followed by another of 2 ml one hour later, after which the column was operated for another 5-6 hours. Then a 4 ml sample was taken from the condenser, followed at once by taking a sample from the still.

The condenser we used in this research is illustrated in Fig. 3. The letter a denotes a 4-ml pocket in which the reflux accumulated, a cross section of the condenser at this point being shown at the right.

The advantages of this condenser are that it makes it possible to tap the entire sample of equilibrium reflux at once, and that the trickling rate does not drop to a very small value or to zero when discards are made (when trickling drops below a certain minimum value, even for a brief period, the choking effect vanishes and the efficiency drops off). The liquid in the pocket is stirred by cautiously blowing air through it once an hour. In our subsequent research we eliminated this blow-through, installing minute openings in the bottom of the pocket so that part of the reflux flowing into the pocket emerged over its top edge, while the rest flowed out below, thus preventing its stagnation in the pocket.

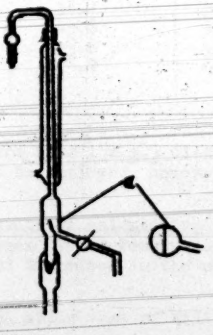

Fig. 3.

The position of the Pulfrich refractometer drum was read off twice for each

* The benzene must have a n_D^{20} of 1.50110, and the carbon tetrachloride a n_D^{20} of 1.4603.

sample. The first reading usually differed from the second one by 0.1'-0.2'. Only another determination with a new batch of the sample yielded a stable result that coincided with subsequent determinations.

As the progress of experiments like those in Table 5 showed, the error in measuring efficiency at high values of the latter may be due to not keeping the column running for a long enough time (until it reaches equilibrium) and to errors in measuring the concentration; all other sources of error are secondary.

Theoretically, the amount of liquid placed in the still to measure efficiency does not affect the latter. In practice, however, the more liquid used, the more accurate the results obtained. Then the tapping of samples from the condenser (for the Abbe refractometer) does not change the concentration in the still perceptibly, and equilibrium samples have a constant refractive index. On the other hand, using very large quantities of solution is inadvisable because of the reagent consumption involved. We usually use 200 ml of solution for 30-50 ml priming charges.

To secure still solutions corresponding to 5, 100, 200, etc., steps (Table 5), we reckoned the initial solutions on the basis of the priming charge (40 ml) plus 8 ml for discards and the contents of the pocket before each sample is taken.

Table 6 contrasts the figures on the number of steps, secured by the foregoing method, with those secured by Method 1 - using the x,y diagram.

TABLE 6

Comparison of the Results of Calculating the Number of Steps from the Step Number - Concentration Diagram and From the x,y Diagram

CCl_4 concentration in the condenser reflux, molar %	Number of steps from the step number - concentration diagram	Number of steps from the x,y diagram	CCl_4 concentration in the condenxer reflux, molar %	Number of steps from the step number - concentration diagram	Number of steps from the x,y diagram
3.0	0.0	0.0	50.0	23.6	23.2
5.0	2.9	2.9	60.0	28.2	27.8
7.5	5.4	5.3	70.0	34.7	34.2
10.0	7.3	7.2	80.0	45.8	45.2
20.0	12.3	12.1	85.0	55.6	53.7
30.0	15.8	15.8	90.0	74.2	67.8
40.0	19.8	19.4			

Table 6 indicates that calculating the number of steps from the x,y diagram yields fairly accurate results up to 45 steps. It cannot be employed, however, for higher efficiencies.

Lastly, we reproduce Table 7, which compares the results of calculating the number of steps for the methylcyclohexane - n-heptane system by the Fenske method [1], the Willingham and Rossini method [2], and the method described in the present paper.

This shows that the Fenske calculation is inaccurate, while that of Willingham and Rossini is quite accurate.

The calculations for Table 2 were checked by P.Ya.Molodenko, while R.V. Lyzlova assisted in the experimental check of this table; I wish to express my indebtedness to them here.

TABLE 7

Comparison of the Results Obtained in Calculating the Number of Steps by the Fenske Method, the Willingham and Rossini Method, and the Method Described in the Present Paper

Methylcyclohexane – n-Heptane System

Molar % n-heptane in still liquid	Molar % n-heptane in condenser reflux	Midpoint of interval, %	α of interval midpoint	Number of steps, n	Σn	Remarks
3.0	96.4	49.7	1.07	100.00	100.00	Calculation by the Fenske method. Value of α by the Fenske method.
3.0	96.4	49.7	1.07482	93.78	93.78	Calculation by the Willingham and Rossini method. The value of α was taken from the Willingham and Rossini data for the midpoint of the concentration interval.
3.0	14.68	8.84	1.07566	23.51		Calculated by dividing into concentration intervals. The values of α were calculated from the Willingham and Rossini data.
14.68	26.35	20.51	1.07543	10.08		
26.35	49.70	38.03	1.07507	14.03		
49.70	73.05	61.38	1.07459	14.02	93.70	
73.05	84.73	78.89	1.07423	10.00		
84.73	96.40	90.56	1.07400	22.06		

SUMMARY

1. A method is described for calculating the number of steps (theoretical plates) in a system with variable α (relative volatility).

2. The benzene – carbon tetrachloride system is proposed for measuring the efficiency of rectifying columns (the number of steps). The number of steps is calculated for this system in the concentration range of 3-99 molar % CCl_4. The results of the computation are set forth in a table which makes it possible to plot step number – concentration diagrams to determine column efficiency.

3. The correctness of the data on the liquid-vapor equilibria in the benzene – carbon tetrachloride system and of the computation of the number of steps has been checked experimentally with a rectifying column. This check has shown that the proposed system can be used to measure the efficiency of columns having as many as 500 steps.

4. The proposed system possesses the following advantages over all others known up to the present time: the constituents are readily available and easy to purify, and concentrations can be determined with high accuracy refractometrically.

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SPECTROPHOTOMETRIC INVESTIGATION OF MAXIMA IN THE COMPOSITION - PROPERTY DIAGRAM WHEN THE SYSTEM CONCENTRATION IS CHANGED IN SOLUTIONS OF COBALT HALIDES

I. INVESTIGATION OF COMPLEX IONS OF COBALT (II) IN ETHYL ALCOHOL

M. S. Barvinok

In determining the composition of the complex ion formed in solution from the constituents A and B according to the equation $\underline{m}A + \underline{n}B = A_{\underline{m}}B_{\underline{n}}$, we have to find $\underline{m}$ and $\underline{n}$, A being a metallic ion and B any molecule or anion, simple or complex. If the complex ion $A_{\underline{m}}B_{\underline{n}}$ has a characteristic color, its composition may be determined by the method of continuous changes, using the optical density as the property tested [1]. The graph of optical density D versus composition must be a curve with a maximum or a minimum $D = D_{observed} = (D_1 + D_2)$ where $D_{observed}$ is the optical density of the system $\underline{m}A + \underline{n}B = A_{\underline{m}}B_{\underline{n}}$ in the solution; D_1 is the optical density of a solution of the constituent A; and D_2 is the optical density of a solution of the constituent B.

The position of the maximum or minimum on the optical density - composition curve is given by the ratio $\underline{m}/\underline{n}$.

The less the complex ion is dissociated in the solution, the sharper will the maximum or the minimum be.

As we know from experiment, the complex ion $A_{\underline{m}}B_{\underline{n}}$ is stable in solution throughout a certain temperature and concentration range. In most instances its dissociation is gradual, as these conditions approach the "boundary" values. That is why the abscissas (composition) of the point on the diagram representing the complex ion $A_{\underline{m}}B_{\underline{n}}$ does not change as the result of a change in the factors governing equilibrium within the region of the stable state, with the exception of rare instances of compounds of variable composition.

If we move from the region where the given complex ion is partially dissociated, by changing these factors, into a region where there is no dissociation, the abscissa of the maximum or minimum representing the complex ion $A_{\underline{m}}B_{\underline{n}}$ asymptotically approaches the point representing the composition of the complex ion $A_{\underline{m}}B_{\underline{n}}$ and stays there during all changes within the stable region. The two parts of the curve on which the maximum or minimum is located meet at an angle that grows more and more acute as we approach the boundary of the stable-state region, and the point becomes more and more distinct.

EXPERIMENTAL

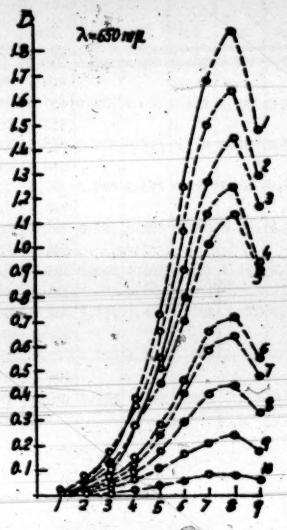
We investigated the $Co(ClO_4)_2$ - LiCl - ethyl alcohol system, making a study of sections parallel to the stable diagonal. For each section we made up a series

of solutions by mixing alcoholic solutions of $Co(ClO_4)_2$ and LiCl of the same molarity in various proportions, keeping the volume unchanged (method of continuous changes [1]). A total of ten series of solutions was investigated at the following aggregate concentrations: 0.1, 0.09, 0.08, 0.07, 0.06, 0.05, 0.04, 0.03, 0.02, and 0.01 mole per liter, the solutions corresponding to the respective sections. The cobalt perchlorate preparation employed was $Co(ClO_4)_2 \cdot 6H_2O$, prepared from chemically pure, nickel-free cobalt carbonate and chemically pure perchloric acid. The solutions of cobalt perchlorate were made up with doubly recrystallized $Co(ClO_4)_2 \cdot 6H_2O$.

Chemically pure lithium chloride was recrystallized twice and desiccated at 110° in a current of HCl. The anhydrous ethyl alcohol was prepared as described in the literature [2].

The optical density was measured with a Beckmann quartz photoelectric spectrophotometer at a temperature of 20 ±1°. The measurement results are listed in Tables 1-10 and shown in the figure. Tables 1-10 likewise indicate the technique of making up the solutions.

As we see in the figure, the peak of the maxima begins to become sharp at an aggregate concentration of 0.03 mole/liter. At an aggregate concentration of 0.01 mole/liter the maximum is extremely flat. As we pass from the solutions of the first series, with an aggregate concentration of 0.1 mole/liter to those of the tenth series, with an aggregate concentration of 0.01 mole/liter, the optical density of the solutions diminishes, owing to the decrease in the concentration of the complex ions in the solutions as the latter are diluted.



Cobalt perchlorate + lithium chloride + ethyl alcohol

Sections parallel to the cobalt perchlorate - lithium chloride side. The composition of the solutions represented by the curves 1-10 is given in the respective tables.

The position of the maxima on the curves of optical density D versus composition at aggregate concentrations of 0.1 to 0.09 mole/liter in the system: $Co(ClO_4)_2$ + LiCl in ethyl alcohol corresponds to a composition of the complex ion in which $m/n = 1:4$, where m is the number of cobalt ions in the complex ion, and n is the number of chlorine ions in the complex ion.

As we have stated before, at this ratio of cobalt to chlorine ions the cobaltochloride complex ions in ethyl alcohol have the composition of $CoCl_4^{--}$ [3]. The abscissa (the composition) of the point in the diagram representing the composition of the complex ion $CoCl_4^{--}$ does not change down to an aggregate concentration of 0.01 mole/liter. At the aggregate concentration of 0.01 mole/liter the maximum becomes so flat that it is hard to determine the composition of the complex ion.

A slight shift of the point representing the composition of the complex ion $CoCl_4^{--}$ along the axis of abscissas (compositions) toward a lower percentage of chlorine ions in the cobaltochloride complex ion is observable, however.

Table 1

Optical Density of Alcoholic Solutions of Cobalt Perchlorate Mixed with Lithium Chloride at an Aggregate Concentration of 0.1 mole.

Solution No.	Solution Composition $Co(ClO_4)_2$ (in ml.)	LiCl (in ml.)	Concentration (moles/liter) $Co(ClO_4)_2$	LiCl	Optical Density $D_{obs.}$ at λ (in mμ) 600	625	650	675	700	$\bar{D}$ at λ (in mμ) 600	625	650	675	700
1	4.5	0.5	0.09	0.01	0.063	0.045	0.043	0.031	0.017	0.005	0.005	0.005	0.001	0.000
I	4.5	0	0.09	-	0.048	0.040	0.038	0.030	0.023					
2	4.0	1.0	0.08	0.02	0.095	0.095	0.098	0.073	0.027	0.052	0.060	0.064	0.046	0.005
II	4.0	0	0.08	-	0.048	0.035	0.034	0.027	0.022					
3	3.5	1.5	0.07	0.03	0.165	0.180	0.193	0.153	0.045	0.127	0.147	0.168	0.127	0.027
III	3.5	0	0.07	-	0.038	0.033	0.030	0.026	0.018					
4	3.0	2.0	0.06	0.04	0.325	0.370	0.418	0.342	0.100	0.294	0.343	0.392	0.323	0.089
IV	3.0	0	0.06	-	0.031	0.027	0.026	0.019	0.011					
5	2.5	2.5	0.05	0.05	0.550	0.650	0.750	0.642	0.195	0.624	0.625	0.726	0.625	0.188
V	2.5	0	0.05	-	0.026	0.025	0.023	0.017	0.012					
6	2.0	3.0	0.04	0.06	0.892	1.080	1.270	1.160	0.382	0.869	1.056	1.252	1.146	0.367
VI	2.0	0	0.04	-	0.023	0.024	0.018	0.014	0.015					
7	1.5	3.5	0.03	0.07	1.200	1.450	1.700	1.580	0.580	1.195	1.435	1.686	1.572	0.576
VII	1.5	0	0.03	-	0.005	0.015	0.014	0.008	0.004					
8	1.0	4.0	0.02	0.08	1.270	1.550	1.900	1.800	0.710	1.258	1.538	1.890	1.794	0.706
VIII	1.0	0	0.02	-	0.012	0.012	0.010	0.008	0.004					
9	0.5	0.5	0.01	0.09	1.000	1.230	1.500	1.500	0.603	0.994	1.222	1.494	1.486	0.603
IX	0.5	0	0.01	-	0.006	0.008	0.006	0.004	0					

Table 2

at an aggregate concentration of 0.09 mole.

1	4.5	0.5	0.081	0.009	0.052	0.044	0.042	0.028	0.017	0.018	0.018	0.020	0.013	0.011
I	4.5	0	0.081	-	0.034	0.026	0.022	0.015	0.006					
2	4.0	1.0	0.072	0.018	0.092	0.088	0.091	0.064	0.025	0.061	0.063	0.070	0.049	0.018
II	4.0	0	0.072	-	0.031	0.025	0.021	0.015	0.007					
3	3.5	1.5	0.063	0.027	0.158	0.171	0.188	0.142	0.043	0.130	0.149	0.170	0.128	0.036
III	3.5	0	0.063	-	0.028	0.022	0.018	0.014	0.007					
4	3.0	2.0	0.054	0.036	0.296	0.336	0.375	0.305	0.090	0.275	0.320	0.360	0.298	0.087
IV	3.0	0	0.054	-	0.023	0.016	0.015	0.007	0.003					
5	2.5	2.5	0.045	0.045	0.495	0.590	0.675	0.589	0.178	0.475	0.575	0.662	0.581	0.178
V	2.5	0	0.045	-	0.020	0.015	0.013	0.008	0.005					
6	2.0	3.0	0.036	0.054	0.770	0.920	1.080	0.950	0.310	0.754	0.909	1.069	0.946	0.308
VI	2.0	0	0.036	-	0.016	0.011	0.011	0.004	0.004					
7	1.5	3.5	0.027	0.063	1.060	1.280	1.500	1.400	0.515	1.048	1.272	1.498	1.393	0.515
VII	1.5	0	0.027	-	0.012	0.008	0.008	0.007	0					
8	1.0	4.0	0.018	0.072	1.170	1.400	1.650	1.610	0.648	1.161	1.394	1.643	1.603	0.648
VIII	1.0	0	0.018	-	0.009	0.006	0.007	0.007	0					
9	0.5	4.5	0.009	0.081	0.882	1.080	1.310	1.330	0.540	0.879	1.078	1.308	1.327	0.540
IX	0.5	0	0.009	-	0.003	0.002	0.002	0.003	0.003					

Table 3

Optical Density of Alcoholic Solutions of Cobalt Perchlorate Mixed with Lithium Chloride

at an Aggregate Concentration of 0.08 mole.

Solution No.	Solution Composition $Co(ClO_4)_2$ (in ml.)	LiCl	Concentration (moles/liter) $Co(ClO_4)_2$	LiCl	Optical Density D_{obs} at λ (in mμ) 600	625	650	675	700	$\bar{D}$ at λ (in mμ) 600	625	650	675	700
1	4.5	0.5	0.072	0.008	0.045	0.038	0.035	0.027	0.013	0.014	0.015	0.013	0.012	0.008
I	4.5	0	0.072	-	0.031	0.023	0.022	0.015	0.010					
2	4.0	1.0	0.064	0.016	0.077	0.073	0.075	0.055	0.018	0.049	0.051	0.054	0.041	0.008
II	4.0	0	0.064	-	0.028	0.022	0.021	0.014	0.010					
3	3.5	1.5	0.056	0.024	0.132	0.142	0.153	0.118	0.034	0.107	0.122	0.135	0.105	0.026
III	3.5	0	0.056	-	0.025	0.020	0.018	0.013	0.008					
4	3.0	2.0	0.048	0.032	0.235	0.268	0.298	0.235	0.067	0.214	0.252	0.284	0.225	0.063
IV	3.0	0	0.048	-	0.021	0.016	0.014	0.010	0.004					
5	2.5	2.5	0.040	0.040	0.418	0.492	0.564	0.465	0.138	0.400	0.478	0.556	0.456	0.134
V	2.5	0	0.040	-	0.018	0.014	0.008	0.009	0.004					
6	2.0	3.0	0.032	0.048	0.650	0.790	0.920	0.800	0.253	0.636	0.779	0.901	0.781	0.249
VI	2.0	0	0.032	-	0.014	0.011	0.009	0.009	0.004					
7	1.5	3.5	0.024	0.056	0.885	1.100	1.220	1.180	0.390	0.875	1.083	1.273	1.179	0.390
VII	1.5	0	0.024	-	0.010	0.007	0.007	0.001	0					
8	1.0	4.0	0.016	0.064	1.000	1.220	1.460	1.430	0.500	0.994	1.216	1.452	1.429	0.500
VIII	1.0	0	0.016	-	0.006	0.004	0.008	0.001	0					
9	0.5	4.5	0.008	0.072	0.780	0.960	1.180	1.180	0.432	0.777	0.958	1.178	1.179	0.432
IX	0.5	0	0.008	-	0.008	0.002	0.002	0.001	0					

Table 4

at an Aggregate Concentration of 0.07 moles

1	4.5	0.5	0.063	0.007	0.038	0.032	0.030	0.023	0.012	0.011	0.010	0.010	0.012	0.005
I	4.5	0	0.063	-	0.027	0.022	0.020	0.011	0.007					
2	4.0	1.0	0.056	0.014	0.068	0.083	0.065	0.042	0.018	0.045	0.043	0.046	0.031	0.011
II	4.0	0	0.056	-	0.023	0.020	0.019	0.011	0.007					
3	3.5	1.5	0.049	0.021	0.125	0.134	0.143	0.108	0.030	0.105	0.117	0.127	0.098	0.024
III	3.5	0	0.049	-	0.020	0.017	0.016	0.010	0.006					
4	3.0	2.0	0.042	0.028	0.228	0.268	0.298	0.229	0.063	0.213	0.251	0.282	0.222	0.062
IV	3.0	0	0.042	-	0.016	0.012	0.011	0.007	0.011					
5	2.5	2.5	0.035	0.035	0.390	0.460	0.527	0.435	0.125	0.376	0.449	0.517	0.428	0.113
V	2.5	0	0.035	-	0.014	0.011	0.010	0.007	0.012					
6	2.0	3.0	0.028	0.042	0.595	0.715	0.810	0.710	0.218	0.582	0.705	0.801	0.703	0.215
VI	2.0	0	0.028	-	0.013	0.010	0.009	0.007	0.003					
7	1.5	3.5	0.021	0.049	0.800	0.970	1.140	1.050	0.359	0.792	0.963	1.137	1.048	0.359
VII	1.5	0	0.021	-	0.008	0.007	0.003	0.002	0					
8	1.0	4.0	0.014	0.056	0.865	1.050	1.250	1.210	0.440	0.858	1.045	1.248	1.208	0.440
VIII	1.0	0	0.014	-	0.007	0.005	0.002	0.002	0					
9	0.5	4.5	0.007	0.063	0.663	0.785	0.948	0.942	0.355	0.857	0.782	0.948	0.940	0.356
IX	0.5	0	0.007	-	0.008	0.003	0.002	0.002	0					

Table 5

Optical Density of Alcoholic Solutions of Cobalt Perchlorate Mixed with Lithium Chloride

at an Aggregate Concentration of 0.06 moles

Solution No.	Solution Composition		Concentration (moles/liter)		Optical Density D_{obs} at λ (in mμ)					$\bar{D}$ at λ (in mμ)				
	$Co(ClO_4)_2$ (in ml.)	LiCl	$Co(ClO_4)_2$	LiCl	600	625	650	675	700	600	625	650	675	700
1	4.5	0.5	0.054	0.006	0.036	0.029	0.028	0.020	0.012	0.015	0.014	0.013	0.009	0.008
I	4.5	0	0.054	-	0.021	0.015	0.015	0.011	0.004					
2	4.0	1.0	0.048	0.012	0.057	0.054	0.055	0.039	0.015	0.038	0.039	0.042	0.028	0.009
II	4.0	0	0.048	-	0.019	0.015	0.013	0.011	0.006					
3	3.5	1.5	0.042	0.018	0.100	0.105	0.113	0.083	0.021	0.083	0.098	0.102	0.074	0.017
III	3.5	0	0.042	-	0.017	0.012	0.011	0.009	0.004					
4	3.0	2.0	0.036	0.024	0.188	0.208	0.285	0.178	0.045	0.174	0.198	0.277	0.172	0.042
IV	3.0	0	0.036	-	0.014	0.010	0.008	0.006	0.003					
5	2.5	2.5	0.030	0.030	0.345	0.406	0.460	0.365	0.104	0.332	0.398	0.452	0.359	0.101
V	2.5	0	0.030	-	0.013	0.010	0.008	0.006	0.003					
6	2.0	3.0	0.024	0.036	0.522	0.620	0.708	0.590	0.172	0.513	0.612	0.702	0.585	0.169
VI	2.0	0	0.024	-	0.009	0.008	0.006	0.005	0.003					
7	1.5	3.5	0.018	0.042	0.717	0.862	1.020	0.892	0.282	0.711	0.858	1.017	0.890	0.282
VII	1.5	0	0.018	-	0.006	0.004	0.003	0.002	0					
8	1.0	4.0	0.012	0.048	0.779	0.945	1.140	1.060	0.358	0.773	0.941	1.137	1.058	0.358
VIII	1.0	0	0.012	-	0.006	0.004	0.003	0.002	0					
9	0.5	4.5	0.006	0.054	0.610	0.730	0.880	0.850	0.300	0.608	0.730	0.878	0.850	0.300
IX	0.5	0	0.006	-	0.002	0	0	0	0					

Table 6

at an Aggregate Concentration of 0.05 moles

1	4.5	0.5	0.045	0.005	0.027	0.022	0.020	0.015	0.008	0.009	0.007	0.008	0.005	0.001
I	4.5	0	0.045	0	0.018	0.015	0.012	0.010	0.007					
2	4.0	1.0	0.040	0.010	0.043	0.040	0.040	0.028	0.011	0.024	0.025	0.027	0.018	0.004
II	4.0	0	0.040	0	0.019	0.015	0.013	0.010	0.007					
3	3.5	1.5	0.035	0.015	0.078	0.081	0.085	0.062	0.018	0.065	0.068	0.072	0.055	0.015
III	3.5	0	0.035	0	0.013	0.013	0.013	0.007	0.008					
4	3.0	2.0	0.030	0.020	0.136	0.152	0.165	0.124	0.030	0.123	0.142	0.157	0.117	0.028
IV	3.0	0	0.030	0	0.013	0.010	0.008	0.007	0.002					
5	2.5	2.5	0.025	0.025	0.227	0.263	0.296	0.232	0.058	0.218	0.255	0.289	0.227	0.058
V	2.5	0	0.025	0	0.009	0.008	0.007	0.005	0					
6	2.0	3.0	0.020	0.030	0.343	0.410	0.468	0.385	0.104	0.336	0.404	0.465	0.386	0.104
VI	2.0	0	0.020	0	0.007	0.006	0.003	0.004	0					
7	1.5	3.5	0.015	0.035	0.465	0.568	0.670	0.570	0.178	0.460	0.565	0.665	0.560	0.177
VII	1.5	0	0.015	0	0.005	0.003	0.003	0.002	0.001					
8	1.0	4.0	0.010	0.040	0.500	0.610	0.722	0.652	0.208	0.495	0.607	0.719	0.650	0.217
VIII	1.0	0	0.010	0	0.005	0.003	0.003	0.002	0.001					
9	0.5	4.5	0.005	0.045	0.380	0.462	0.560	0.530	0.186	0.378	0.462	0.560	0.530	0.186
IX	0.5	0	0.005	0	0.002	0	0	0	0					

Table 7

Optical Density of Alcoholic Solutions of Cobalt Perchlorate Mixed with Lithium Chloride

at an Aggregate Concentration of 0.04 moles.

Solution No.	Solution Composition $Co(ClO_4)_2$ (in ml.)	LiCl (in ml.)	Concentration (moles/liter) $Co(ClO_4)_2$	Concentration (moles/liter) LiCl	Optical Density D_{obs} at λ (in mμ) 600	625	650	675	700	D at λ (in mμ) 600	625	650	675	700
1	4.5	0.5	0.036	0.004	0.022	0.019	0.024	0.013	0.006	0.001	0.004	0.009	0.002	0.002
I	4.5	0	0.036	-	0.021	0.015	0.015	0.011	0.004					
2	4.0	1.0	0.032	0.008	0.035	0.033	0.033	0.024	0.006	0.016	0.018	0.020	0.013	0
II	4.0	0	0.032	-	0.019	0.015	0.013	0.011	0.006					
3	3.5	1.5	0.028	0.012	0.065	0.068	0.074	0.052	0.008	0.048	0.056	0.063	0.043	0.008
III	3.5	0	0.028	-	0.017	0.012	0.011	0.009	0.005					
4	3.0	2.0	0.024	0.016	0.114	0.126	0.140	0.108	0.024	0.100	0.116	0.132	0.097	0.021
IV	3.0	0	0.024	-	0.014	0.010	0.008	0.006	0.003					
5	2.5	2.5	0.020	0.020	0.198	0.230	0.260	0.197	0.046	0.185	0.220	0.252	0.191	0.043
V	2.5	0	0.020	-	0.013	0.010	0.008	0.006	0.003					
6	2.0	3.0	0.016	0.024	0.310	0.370	0.423	0.384	0.082	0.301	0.362	0.417	0.379	0.079
VI	2.0	0	0.016	-	0.009	0.008	0.006	0.005	0.003					
7	1.5	3.5	0.012	0.028	0.420	0.512	0.593	0.502	0.148	0.414	0.508	0.590	0.502	0.148
VII	1.5	0	0.012	-	0.006	0.004	0.003	0	0					
8	1.0	4.0	0.008	0.032	0.447	0.550	0.648	0.579	0.185	0.441	0.546	0.645	0.577	0.185
VIII	1.0	0	0.008	-	0.006	0.004	0.003	0.002	0					
9	0.5	4.5	0.004	0.036	0.338	0.410	0.488	0.452	0.152	0.336	0.410	0.486	0.450	0.152
IX	0.5	0	0.004	-	0.002	0	0.002	0.002	0					

Table 8

at an Aggregate Concentration of 0.03 moles

1	4.5	0.5	0.027	0.003	0.020	0.012	0.010	0.017	0.004	0.007	0.002	0.007	0.007	0.004
I	4.5	0	0.027	-	0.013	0.010	0.003	0	0					
2	4.0	1.0	0.024	0.006	0.027	0.023	0.024	0.017	0.006	0.014	0.013	0.021	0.017	0.006
II	4.0	0	0.024	-	0.013	0.010	0.003	0	0					
3	3.5	1.5	0.021	0.009	0.047	0.045	0.050	0.033	0.006	0.039	0.037	0.048	0.033	0.002
III	3.5	0	0.021	-	0.008	0.008	0.002	0	0					
4	3.0	2.0	0.018	0.012	0.078	0.088	0.096	0.067	0.016	0.065	0.085	0.091	0.065	0.016
IV	3.0	0	0.018	-	0.013	0.003	0.005	0.002	0					
5	2.5	2.5	0.015	0.015	0.139	0.165	0.186	0.136	0.030	0.126	0.162	0.184	0.136	0.030
V	2.5	0	0.015	-	0.013	0.003	0.002	0	0					
6	2.0	3.0	0.012	0.018	0.215	0.260	0.295	0.225	0.052	0.208	0.258	0.295	0.225	0.052
VI	2.0	0	0.012	-	0.007	0.002	0	0	0					
7	1.5	3.5	0.009	0.021	0.285	0.350	0.408	0.333	0.093	0.282	0.350	0.408	0.333	0.093
VII	1.5	0	0.009	-	0.003	0	0	0	0					
8	1.0	4.0	0.006	0.024	0.300	0.370	0.439	0.378	0.112	0.297	0.370	0.439	0.378	0.112
VIII	1.0	0	0.006	-	0.003	0	0	0	0					
9	0.5	4.5	0.003	0.027	0.230	0.285	0.338	0.303	0.093	0.229	0.285	0.338	0.303	0.093
IX	0.5	0	0.003	-	0.001	0	0	0	0					

Table 9

Optical Density of Alcoholic Solutions of Cobalt Perchlorate Mixed with Lithium Chloride

at an Aggregate Concentration of 0.02 moles

Solution No.	Solution Composition: $Co(ClO_4)_2$ (in ml.)	LiCl	Concentration (moles/liter): $Co(ClO_4)_2$	LiCl	Optical Density D_{obs} at λ (in mμ): 600	625	650	675	700	$\bar{D}$ at λ (in mμ): 600	625	650	675	700
1	4.5	0.5	0.018	0.002	0.013	0.011	0.010	0.008	0.005	0.004	0.006	0.008	0.008	0.005
I	4.5	0	0.018	-	0.009	0.005	0.002	0	0					
2	4.0	1.0	0.016	0.004	0.021	0.018	0.018	0.012	0.005	0.012	0.013	0.016	0.012	0.005
II	4.0	0	0.016	-	0.009	0.005	0.002	0	0					
3	3.5	1.5	0.014	0.006	0.028	0.028	0.028	0.018	0.004	0.019	0.023	0.026	0.018	0.004
III	3.5	0	0.014	-	0.009	0.005	0.002	0	0					
4	3.0	2.0	0.012	0.008	0.055	0.057	0.063	0.042	0.010	0.047	0.053	0.063	0.042	0.010
IV	3.0	0	0.012	-	0.008	0.004	0	0	0					
5	2.5	2.5	0.010	0.010	0.090	0.100	0.110	0.077	0.017	0.083	0.097	0.110	0.077	0.017
V	2.5	0	0.010	-	0.007	0.003	0	0	0					
6	2.0	3.0	0.008	0.012	0.127	0.146	0.165	0.118	0.025	0.122	0.144	0.165	0.118	0.025
VI	2.0	0	0.008	-	0.005	0.002	0	0	0					
7	1.5	3.5	0.006	0.014	0.164	0.202	0.229	0.176	0.040	0.162	0.202	0.209	0.176	0.040
VII	1.5	0	0.006	-	0.003	0	0	0	0					
8	1.0	4.0	0.004	0.016	0.174	0.214	0.245	0.198	0.056	0.171	0.214	0.245	0.198	0.056
VIII	1.0	0	0.004	-	0.003	0	0	0	0					
9	0.5	4.5	0.002	0.018	0.127	0.160	0.185	0.155	0.043	0.124	0.160	0.185	0.155	0.043
IX	0.5	0	0.002	-	0.003	0	0	0	0					

Table 10

at an Aggregate Concentration of 0.01 moles

1	4.5	0.5	0.009	0.001	0.005	0.006	0.003	0.003	0.001	0.005	0.006	0.008	0.008	0.001
I	4.5	0	0.009	-	0	0	0	0	0					
2	4.0	1.0	0.008	0.002	0.007	0.008	0.008	0.004	0.001	0.007	0.008	0.008	0.004	0.001
II	4.0	0	0.008	-	0	0	0	0	0					
3	3.5	1.5	0.007	0.003	0.008	0.011	0.009	0.005	0.000	0.008	0.011	0.009	0.005	0
III	3.5	0	0.007	-	0	0	0	0	0					
4	3.0	2.0	0.006	0.004	0.018	0.022	0.024	0.015	0.002	0.018	0.022	0.024	0.015	0.002
IV	3.0	0	0.006	-	0	0	0	0	0					
5	2.5	2.5	0.005	0.005	0.031	0.033	0.042	0.028	0.003	0.031	0.033	0.042	0.028	0.003
V	2.5	0	0.005	-	0	0	0	0	0					
6	2.0	3.0	0.004	0.006	0.045	0.055	0.062	0.043	0.005	0.045	0.055	0.062	0.043	0.005
VI	2.0	0	0.004	-										
7	1.5	3.5	0.003	0.007	0.060	0.073	0.085	0.061	0.018	0.060	0.073	0.085	0.061	0.018
VII	1.5	0	0.003	-										
8	1.0	4.0	0.002	0.008	0.059	0.073	0.086	0.063	0.017	0.059	0.073	0.086	0.068	0.017
VIII	1.0	0	0.002	-	0	0	0	0	0					
9	0.5	4.5	0.001	0.009	0.041	0.056	0	0.043	0.011	0.041	0.056	0.070	0.043	0.011
IX	0.5	0	0.001	-	0	0	0	0						

SUMMARY

1. The position of the maxima on the curves of the optical density, $\bar{D}$, versus the composition of the system: $Co(ClO_4)_2$ + LiCl in ethyl alcohol has been investigated for various sections parallel to a stable diagonal.

The triangle sections have been investigated at aggregate concentrations of the cobalt perchlorate plus the lithium chloride in ethyl alcohol ranging from 0.1 to 0.01 mole/liter.

2. The maxima on the optical density - composition curves are located at a position corresponding to a composition of the complex ion in which $m/n = 1:4$.

3. The sharpness of the maxima on the optical density - composition curves does not vary appreciably down to an aggregate concentration of 0.03 mole/liter.

At an aggregate concentration of 0.01 mole/liter the maximum becomes so flat as to render determination of the composition of the complex ion impossible.

A slight shift of the point representing the composition of the $CoCl_4^{--}$ complex ion is observed, however, along the axis of abscissas (compositions), in the direction of a lower percentage of chlorine ions in the cobalto(II)-chloride complex ion.

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July 24, 1949.

THE BINARY SYSTEMS CONSTITUTED BY $SnCl_4$, $SbCl_3$ and $AsCl_3$

IV. THE $SbCl_3$ - $CH_2ClCOOH$ SYSTEM

M. Usanovich and T. Sumarokova

The conductance, viscosity, and density of the $SbCl_3$ - $CH_2ClCOOH$ system have been investigated at 50, 60, and 70°, and its fusibility curve has been plotted.

The measurements of viscosity are listed in Table 1, with the variation of viscosity with composition shown graphically in Fig. 1.

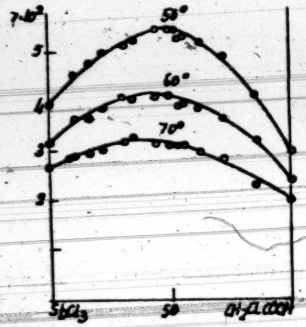

Fig. 1.

TABLE 1

Viscosity of the $SbCl_3$ - $CH_2ClCOOH$ System

Molar % $SbCl_3$	$\eta \times 10^2$		
	50°	60°	70°
100.00	3.926	3.147	2.660
90.19	–	–	2.829
89.30	4.500	3.615	2.898
83.10	4.757	3.687	2.952
77.54	4.987	3.871	3.082
68.81	5.160	4.075	3.211
65.21	5.244	4.066	3.270
56.26	5.418	4.089	3.152
50.03	5.457	4.109	3.169
49.08	5.449	–	–
46.48	5.272	3.971	3.155
45.11	5.302	3.993	3.136
37.38	5.154	3.890	2.962
27.85	4.894	3.690	2.865
14.76	4.147	3.202	2.399
0.00	3.021	2.446	2.046

Inspection of Fig. 1 shows that the viscosity isotherms pass through a maximum at 50 mol.% $SbCl_3$. The position of the maximum shifts toward the more viscous constituent, $SbCl_3$, as the temperature is raised. The presence of a maximum on the viscosity isotherms is evidence of the formation of a compound with the composition of $SbCl_3 \cdot CH_2ClCOOH$.

The data on conductance are listed in Table 2. The specific conductance is plotted in Fig. 2 as a function of the composition. The conductance isotherms are of irregular shape. As we see in Fig. 2, the specific conductance rises rather steeply from 100% $SbCl_3$, passing through a maximum at 65 mol% $SbCl_3$. There is a point of inflection on the isotherms at 40-50 mol.% $SbCl_3$, the drop in conductance being slowed down somewhat, but becoming very rapid after 30 mol.% $SbCl_3$. As the temperature is lowered, the maximum conductance shifts toward the $SbCl_3$ side, while the point of inflection shifts toward the equimolecular compound.

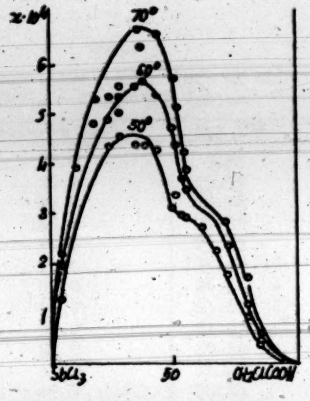

Fig. 2.

TABLE 2

Conductance of the $SbCl_3$ – $CH_2ClCOOH$ System

Mol.% $SbCl_3$	x x 10^4		
	50°	60°	70°
96.10	1.295	1.982	2.147
90.19	–	–	3.957
82.40		4.843	5.324
76.46	4.348	4.909	5.324
71.78	4.600	5.058	5.558
65.21	4.433	5.586	6.750
62.86	4.386	5.702	6.383
56.26	4.322	5.457	6.607
50.03	3.151	4.775	5.762
49.08	3.390	4.404	5.187
46.45	2.993	3.737	4.219
45.11	2.948	3.486	3.899
37.38	2.705	–	–
33.41	2.255	–	–
27.85	1.744	2.398	2.868
20.26	0.982	1.155	1.429
14.76	0.377	0.472	0.544

It seems to us that the point of inflection on the isotherms we secured is caused by the formation of a compound with the composition of $SbCl_3 \cdot CH_2ClCOOH$. This supposition is particularly reinforced by the fact that the inflection point shifts toward the equimolecular compound as the temperature goes down, and had we been able to measure the conductance at lower temperatures, the conductance isotherms would have had to exhibit a minimum representing the composition of the compound $SbCl_3 \cdot CH_2ClCOOH$. A similar picture is observed in many systems; a minimum is exhibited on the conductance isotherms of the $SbCl_3$ – $(C_2H_5)O$ system [1] in particular, as the temperature is lowered.

Thus, as the temperature drops, the curves of specific conductance approach the shape of the curves secured by N.A. Trifonov [2] and his coworkers for systems in which stable compounds are formed. As before, we applied a viscosity correction to the conductance values. The data on the calculation of the corrected conductance * at 50° are listed in Table 3.

The data of Table 3 were used to plot the curve showing the corrected conductance as a function of the composition (Fig. 3).

The shape of the isotherm of corrected conductance is about that of the specific conductance isotherm. Eliminating the effect of viscosity upon conductance did not eliminate the point of inflection, which reflects the formation of a compound of equimolecular composition. The maximum on the curve of corrected conductance occurs at a rational component ratio (67 mol.% $SbCl_3$), representing the composition of the compound $2SbCl_3 \cdot CH_2ClCOOH$. Thinking that the temperature coefficient would enable us to judge the composition of the chemical compounds, we computed the temperature coefficient of conductance. The data on the temperature coefficient of conductance are given in Table 4, while Fig. 4 shows the temperature coefficient of conductance as a function of the composition.

We see in Table 4 that the temperature coefficient of conductance of our

* The correction was applied to the smooth curve.

system is small, varying with the concentration within rather narrow limits.

The values of the temperature coefficient are so small in the region of each of the two constituents as to make them extremely sensitive to experimental error, so that we do not consider these values reliable and do not cite them.

There is no doubt that the maximum of the temperature coefficient of conductance is located at 50 mol.% $SbCl_3$ representing the compound $SbCl_3 \cdot CH_2ClCOOH$. If we assume that the entire curve is

TABLE 3

Corrected Conductance of the $SbCl_3$ – $CH_2ClCOOH$ System

Molar % $SbCl_3$	$\varkappa \times 10^6$
95.0	7.35
90.0	13.05
85.0	17.38
80.0	21.56
75.0	23.12
70.0	23.69
67.0	24.04
60.0	23.69
55.0	21.73
53.0	20.10
50.0	16.69
45.0	15.15
40.0	14.47
35.0	12.38
30.0	9.55
25.0	6.75
20.0	4.24
15.0	2.90
10.0	0.84

TABLE 4

Temperature coefficient of conductance

Mol.% $SbCl_3$	α (in %)
85.0	1.81
80.0	1.92
75.0	2.01
70.0	2.01
65.0	2.15
60.0	2.57
55.0	3.00
50.0	3.60
45.0	2.04
40.0	1.34

Fig. 3.

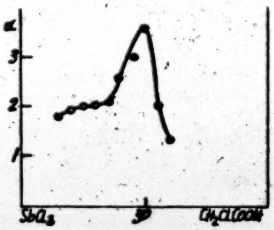

Fig. 4.

significant, then it contains an indication of the existence of another compound, $2SbCl_3 \cdot CH_2ClCOOH$ (point of inflection on the curve). This agrees with the shape of the isotherm of corrected conductance.

The results of our density measurements are given in Table 5.

In Fig. 5 we have plotted the specific volume as a function of the composition

TABLE 5

Density of the $SbCl_3$ – $CH_2ClCOOH$ System

Percent $SbCl_3$		Density		
Molar	By wt.	50°	60°	70°
100.0	100.00	2.7352	2.7148	2.6830
90.19	95.64	2.6319	2.6165	2.5918
89.30	95.27	2.6196	2.5973	2.5769
83.10	92.23	2.5519	2.5386	2.5206
77.54	89.29	2.4890	2.4660	2.4479
68.81	84.20	2.3840	2.3621	–
65.21	81.91	2.3419	2.3188	2.2985
56.26	75.55	2.2253	2.2044	2.1803
50.03	70.70	2.1066	2.0815	2.0726
46.48	67.69	2.0987	2.0791	2.0605
45.11	66.51	2.0805	2.0588	2.0420
37.38	59.07	1.9718	1.9554	1.9370
27.85	48.88	1.8309	1.8133	1.7974
14.76	29.48	1.6309	1.6182	1.6000
0.00	0.00	1.3907	1.3777	1.3042

TABLE 6

Fusibility of the $SbCl_3$ – $CH_2ClCOOH$ System

Molar % $SbCl_3$	Arrest points	
	First	Second
100.00	73.2	–
92.66	67.5	46.0
79.05	56.0	–
76.54	51.3	46.0
69.53	46.5	–
65.56	47.3	46.0
56.26	47.0	29.0
50.03	47.5	–
37.38	27.5	37.5
31.20	41.0	–
24.95	46.5	–
9.74	57.5	–
0.00	63.5	–

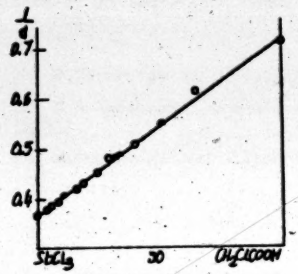

Fig. 5.

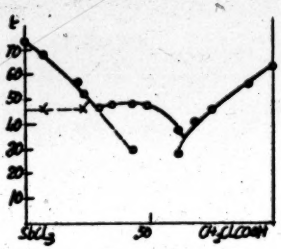

Fig. 6

(in per cent by weight). Inspection of the figure shows that the variation of the specific volume with composition is linear.

The data on fusibility are given in Table 6.

The fusibility diagram of the $SbCl_3$ – $CH_2ClCOOH$ system is reproduced in Fig. 6. The compound $SbCl_3 \cdot CH_2ClCOOH$ is represented in the diagram as an indistinct dystectic maximum. The melting point of the compound $SbCl_3 \cdot CH_2ClCOOH$ is 47.5°.

The eutectic points on the fusibility diagram are located at 72 and 35 mol.% $SbCl_3$ and 46 and 35°, respectively. The first eutectic corresponds to the arrest point at the left of the figure; we did not observe eutectic arrest points in the right half of the diagram.

On the cooling curve of a mixture containing 37.38 mol.% $SbCl_3$ we observed two arrest points, one at 27.5°, and the other at 37.5°. Obviously, monochloracetic acid began to crystallize out as the mixture was cooled, subsequently making way for the crystallization of the compound $SbCl_3 \cdot CH_2ClCOOH$. Thus, the

crystallization curve of $CH_2ClCOOH$ may be prolonged to 27.50 mol.%; this is shown in the diagram by the dashed line.

We also observed two arrest points on the cooling curve of a mixture containing 56.26 mol.% $SbCl_3$: at 47°, corresponding to the crystallization of the compound $SbCl_3 \cdot CH_2ClCOOH$, and at 29°; the latter lies on an extension of the crystallization curve of $SbCl_3$ and is so designated by a dashed line.

Summing up the results of our investigation of the $SbCl_3$ – $CH_2ClCOOH$ system, we note that chemical action does take place in this system. A compound of equimolecular composition is indicated on the curves for all the properties we have investigated. As for the compound $2SbCl_3 \cdot CH_2ClCOOH$, it is reflected only in the diagram of corrected conductance. The structure of the compound is obviously similar to that of the compounds of $SbCl_3$ and CH_3COOH [3].

SUMMARY

1. The conductance, viscosity, and density of the $SbCl_3$ – $CH_2ClCOOH$ system have been investigated at 50, 60, and 70°.

2. The conductance and viscosity diagrams indicate the existence of the compounds $SbCl_3 \cdot CH_2ClCOOH$, and $2SbCl_3 \cdot CH_2ClCOOH$.

3. The fusibility of the $SbCl_3$–$CH_2ClCOOH$ system has been investigated. The fusibility diagram shows the existence of a compound of equimolecular composition as an indistinct dystectic maximum.

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THE BINARY SYSTEMS CONSTITUTED BY $SnCl_4$, $SbCl_3$ and $AsCl_3$

V. THE $SbCl_3$ - CCl_3COOH SYSTEM

T. Sumarokova and M. Usanovich

The conductance, viscosity, and density of the $SbCl_3$ – CCl_3COOH system have been investigated at 50, 60, and 70°, and its fusibility diagram has been plotted.

The viscosity data are listed in Table 1 and plotted graphically in Fig. 1.

TABLE 1

Viscosity of the $SbCl_3$ – CCl_3COOH system

Molar % $SbCl_3$	$\eta \cdot 10^2$		
	50°	60°	70°
100.00	3.926	3.147	2.660
80.32	4.119	3.236	2.642
71.99	4.179	3.312	2.687
49.03	4.377	3.428	2.762
30.07	4.603	3.640	2.870
18.07	4.705	3.735	2.960
4.21	4.806	3.811	3.113
0.00	4.824	3.815	3.033

Fig. 1.

The viscosity diagrams are concave upward, but the sag is not very prominent, as the viscosities of the two constituents do not differ very much.

The conductance data are listed in Table 2.

Fig. 2.

TABLE 2

Conductance of the $SbCl_3$ – CCl_3COOH System

Molar % $SbCl_3$	$\kappa \cdot 10^5$		
	50°	60°	70°
94.61	1.515	1.747	–
82.16	2.005	2.662	3.157
80.32	2.310	2.474	3.389
71.99	2.400	2.960	–
58.07	2.150	2.700	3.449
49.03	1.296	1.648	2.009
40.00	0.590	0.723	1.077
30.07	0.268	0.344	0.430
18.07	–	–	0.249

The specific conductance is plotted as a function of the composition in Fig. 2.

The conductance isotherms exhibit a maximum at about 70 mol.% $SbCl_3$. As the temperature is raised, the conductance rises, while its maximum is shifted toward the trichloroacetic acid. Correcting the conductance for viscosity does not change the shape of the specific conductance curve, but the maximum on the curve of corrected conductance now lies at 67 mol.% $SbCl_3$ and does not shift as the temperature is changed (Fig. 3).

The results of our computation of the corrected conductance are shown in Table 3.

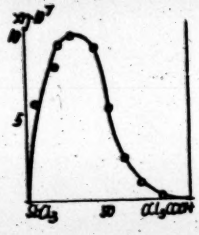

Fig. 3.

Fig. 4.

TABLE 3

Corrected Conductance of the $SbCl_3$ – CCl_3COOH System

Mol. % $SbCl_3$	$\varkappa\eta \cdot 10^7$	
	50°	60°
94.61	6.044	5.515
82.16	8.180	8.778
80.32	9.510	–
71.99	10.030	9.916
58.07	9.210	9.130
49.03	5.670	5.650
40.00	2.660	2.567
30.07	1.230	1.252
18.07	0.280	0.562

TABLE 4

Temperature Coefficient of Conductance

Mol.% $SbCl_3$	α (in %)
90.0	1.66
80.0	1.70
75.0	1.84
70.0	1.98
65.0	2.14
60.0	2.22
55.0	2.28
50.0	2.33
45.0	2.22
40.0	2.12
30.0	2.00

We note in Table 3 that there is very little difference between the values of the corrected conductance for 50 and 60°.

The values of the temperature coefficient, calculated from the smooth curve of specific conductance between the temperatures of 50 and 60°, are listed in Table 4.

The variation of the temperature coefficient of conductance with composition is shown graphically in Fig. 4. As we see from the figure, the temperature coefficient of conductance fluctuates between 1.66 and 2.3%, so that, al

although we give the temperature coefficient, the maximum of which corresponds to a compound of equimolecular composition, we do not attach much significance to this curve.

The density of the $SbCl_3$ – CCl_3COOH system is given in Table 5.

TABLE 5

Density of the $SbCl_3$ – CCl_3COOH System

Per cent $SbCl_3$		Density		
Molar	By Wt.	50°	60°	70°
100.00	100.00	2.7352	2.7148	2.6830
80.32	85.07	2.4784	2.4517	2.4388
58.07	65.92	2.2088	2.1905	2.1755
40.00	48.21	2.0094	1.9915	1.9759
18.0	23.46	1.7870	1.7706	1.7565
0.00	0.00	1.6156	1.6070	1.5864

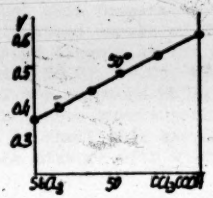

Fig. 5.

The variation of the specific volume with the composition (in per cent by weight) is shown in Fig. 5.

As we see in Fig. 5, the specific volume is a linear function of composition.

A comparison of our viscosity and conductance findings leads us to conclude that chemical reaction takes place in this system. As we have seen, the diagrams reflect the compounds $2SbCl_3 \cdot CCl_3COOH$ and $SbCl_3 \cdot CCl_3COOH$.

We likewise investigated the fusibility of our system, the results being given in Table 6.

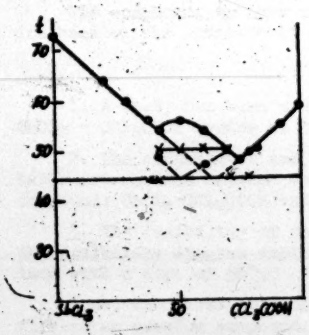

Fig. 6.

TABLE 6

Fusibility of the $SbCl_3$ – CCl_3COOH System

Mol.% $SbCl_3$	Arrest points		
	First	Second	Third
100.00	73.2	–	–
80.32	64.0	–	–
71.99	60.0	46.0	–
62.30	56.0	44.0	48.0
59.48	54.5	44.0	–
58.07	53.5	44.0	50.5
49.03	56.0	50.5	–
40.0	54.0	50.5	–
30.07	51.0	–	–
25.40	48.0	40.0	–
21.90	49.5	44.5	–
18.00	50.5	–	–
7.38	54.5	–	–
0.0	58.5	–	–

The fusibility diagram is reproduced in Fig. 6. This diagram exhibits a dystectic maximum representing the compound $SbCl_3 \cdot CCl_3COOH$ with a m.p. of 56°, and two eutectics, located at 58 and 26 mol.%, with m.p. of 53.5 and 48°,

respectively. The cooling curves for 71.99, 62.30, 59.48, 58.07, and 21.91 mol.% $SbCl_3$ exhibit arrest points at 44°, the arrest point at [illegible] preceding critical points that represent the crystallization of the compound $SbCl_3 \cdot CCl_3COOH$ out of the mixtures containing 62.30, 59.48, and 58.07 mol.% $SbCl_3$. We believe that these critical points represent the crystallization of the eutectic with a m.p. of 44°, located in the metastable region and having 40 mol.% $SbCl_3$. The existence of this eutectic is also borne out by the fact that this temperature and composition correspond to the point where the crystallization curves of $SbCl_3$ and CCl_3COOH intersect, indicated in the figure by dashed lines. As for the thermal arrest points at 50° for the mixtures containing 58.07, 49.03, 40.0, and 30.07 mol.% $SbCl_3$, they may be due to the existence of the compound $SbCl_3 \cdot CCl_3COOH$ in two modifications. We plotted a Tammann diagram for these arrest points, represented in the diagram by dot-dash lines (–·–·–), to check this assumption. The duration of these arrest points was longest for the mixture with 49.03 mol.% $SbCl_3$, which bore out our assumption.

To sum up the results of our research, the diagrams of conductance, viscosity, and fusibility lead us to conclude that acid-base interaction occurs in this system, resulting in the formation of the compounds $SbCl_3 \cdot CCl_3COOH$ and $2SbCl_3 \cdot CCl_3COOH$. The composition of these compounds resembles that of the compounds of $SbCl_3$ with CH_3COOH and $CH_2ClCOOH$ [1,2]; their structure is obviously similar as well.

We consider the interaction of $SbCl_3$ with CCl_3COOH to be acid-basic for the following reasons, which we believe to be beyond cavil. The $SbCl_3$ – CCl_3COOH system is a conductor; the dissociation of the CCl_3COOH is precluded by the absence of a proton acceptor; hence, the $SbCl_3$ dissociates. The $SbCl_2$ cation cannot exist independently, however, and adds a molecule of CCl_3COOH owing to additional valence of the oxygen atom. The CCl_3COOH thus acts as an oxonium compound, while $SbCl_3$ acts as an acid. The same conclusions follow from consideration of the diagram of the dissociation of the coordination compound $SbCl_3 \cdot CCl_3COOH$, since the only possible anion in this case is Cl. It is highly interesting that none of the protonic acids, with the sole exceptions of H_2SO_4 [3], and $HClO_4$ [4], convert CCl_3COOH into an oxonium compound.

The compounds we have synthesized are, as far as we know, the first known instance of the addition of CCl_3COOH as an additive, that is, an oxonium base.

SUMMARY

1. A study has been made of the conductance, viscosity, and density of the $SbCl_3$ – CCl_3COOH system at 50, 60, and 70°.

2. The conductance and viscosity diagrams indicate the existence of acid-basic interaction between the system constituents. The diagrams reflect the compounds $SbCl_3 \cdot CCl_3COOH$ and $2SbCl_3 \cdot CCl_3COOH$.

3. The fusibility of the $SbCl_3$ – CCl_3COOH system has been investigated. The fusibility diagram exhibits the compound $SbCl_3 \cdot CCl_3COOH$ as a dystectic maximum with a m.p. of 56°.

Thus, the first instance has been discovered of CCl_3COOH acting as an additive or an oxonium compound.

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*See CB translation p. 1083 ff.
**See CB translation p. 1323 ff.

ELECTROLYTIC BRASSPLATING FROM NON-CYANIDE SOLUTIONS

A. I. Stabrovsky

Various prescriptions for noncyanide baths have been suggested as replacements for cyanide salts in brassplating baths. Donald [1], proposed a bath containing a high percentage of sodium thiosulfate for the deposition of copper and its alloys at the cathode. Darlington [2] deposited a brass alloy on the cathode from an ammoniacal solution containing the tartrates or oxalates of the metals to be deposited. Tumanov [3] proposed the use of an ammoniacal bath for brassplating. G. Dorini [4] gave a formula for a brassplating bath containing ammonium lactate. Sukhodsky and his associates [5] have shown that brass may be deposited on the cathode from alkaline baths that contain tartrates.

Notwithstanding the variety of formulas suggested for noncyanide baths, none of them has been applied industrially up to the present time; we were therefore interested in making a more detailed study of solutions of various noncyanide coordination compounds of copper and zinc, with the objective of determining the feasibility of brassplating without cyanides. We used as our research objects solutions of copper and zinc chlorides, thiocyanates, and thiosulfates, with glycerol and Rochelle salt, as well as with ammonia, pyrophosphates, and oxalates.

EXPERIMENTAL

1. The conditions governing the cathodic deposition of brass. The deposition of brass at the cathode from noncyanide solutions requires that the reversible electrode potentials of copper and zinc, as well as the deposition potentials of these metals, be made similar. The reversible electrode potentials may be brought closer together by the formation of complex ions, as is the case with the cyanides. The deposition potentials may be brought closer together by setting up a difference in the rate of increase of cathodic depolarization of copper and zinc during electrolysis. The depolarizing effect of the heat of formation of a copper-zinc solid solution likewise promotes the rapprochement of the deposition potentials.

2. Rapprochement of the reversible electrode potentials of copper and zinc by means of the formation of coordination compounds. In aqueous solutions, complex salts are dissociated into ions and conduct electricity like simple salts, so that they, too, are electrolytes. The dissociation of complex salts into ions takes place in two stages. The initial dissociation involves the formation of complex ions; the secondary dissociation entails the appearance of simple ions of the metal in the solution. The following reaction may serve as an instance of the secondary dissociation of complex ions into their component parts:

$$Cu(NH_3)_4^{++} \rightleftharpoons Cu^{++} + 4NH_3 \qquad (1)$$

The equilibrium constant of this reaction, called the instability constant,

is a measure of the decomposition of the complex ion into its constituents and is defined as the ratio of the product of the activities of the resulting ions to the activity of the complex ions, i.e.:

$$\frac{a_{Cu^{++}} \cdot a^4_{NH_3}}{a_{Cu(NH_3)_4^{++}}} = K. \qquad (2)$$

At constant concentrations of the central atom in the coordination compound (copper) and of the coordinated group (ammonia), the size of the instability constant is proportional to the concentration of active simple ions of the metal in the solution. We see from Equation (2) that the magnitude of the instability constant may be readily calculated, once we know the activity of the simple copper ions in the solution, since the activities of the other substances entering into the equation may be found in the appropriate handbooks.

The activity of simple ions of copper or zinc in solutions of their complex was determined by measuring the emf of concentration cells. The activities are then calculated from the equation:

$$E = \frac{RT}{nF} \ln \frac{a_1}{a_2}, \qquad (3)$$

where a_1 is the activity of the metal ions in a solution of a simple salt, and a_2 is the activity of the same ions in the complex salt solution. The results of our determinations of the instability constants are listed in Table 1.

TABLE 1

Instability Constants of Complex Ions of Copper and Zinc (18°C).

No.	Formula of the coordination compound	Concentration of the central atom in the coordination compound, moles/liter	Concentration of the coordinated group, moles/liter	Instability constant
1	K_2CuCl_3	0.05	0.672	$5.01 \cdot 10^{-6}$
2	$Na_6Cu(P_2O_7)_2$.....	0.05	0.100	$3.10 \cdot 10^{-10}$
3	$Na_2Cu(C_2O_4)_2$	0.01	0.040	$2.05 \cdot 10^{-10}$
4	$Na_3Cu(S_2O_3)_2$	0.05	0.100	$2.05 \cdot 10^{-12}$
5	$KCu(CNS)_2$	0.05	3.090	$7.83 \cdot 10^{-13}$
6	$NaCu(C_3H_5O_3)$	0.05	0.100	$4.20 \cdot 10^{-13}$
7	$K_2Cu(C_4H_2O_8)$	0.05	0.075	$6.72 \cdot 10^{-14}$
8	$Cu(NH_3)_4SO_4$	0.05	0.600	$4.85 \cdot 10^{-15}$
9	$K_2Cu(CN)_3$	0.05	0.150	$1.66 \cdot 10^{-21}$
10	$Na_6Zn(P_2O_7)_2$	0.05	0.100	$5.74 \cdot 10^{-8}$
11	$Na_4Zn(C_2O_4)_3$	0.01	0.030	$7.05 \cdot 10^{-9}$
12	$Zn(NH_3)_4SO_4$	0.05	0.600	$4.27 \cdot 10^{-10}$
13	$K_2Zn(CN)_4$	0.05	0.200	$2.52 \cdot 10^{-13}$
14	$Na_2Zn(OH)_4$	0.05	0.670	$3.35 \cdot 10^{-15}$

We see in Table 1 that the instability constant of complex copper ions is smaller than the instability constant of complex zinc ions in pyrophosphate, oxalate, ammoniacal, and cyanide solutions. Hence, the concentration of simple copper ions in these solutions will be lower than the concentrations of simple zinc ions.

This indicates that the active concentrations of simple ions of Cu and Zn may vary over a wide range in different solutions, depending upon the nature of the complex salts. Inasmuch as the reversible electrode potential depends upon the active concentration of simple ions of the metal, we can bring the reversible electrode potentials of copper and zinc closer together or farther apart by changing the concentration of the metal's ions in the solution as the result of the formation of a coordination compound. In measuring the reversible electrode potentials of copper and zinc in solutions of complex salts, we used the concentrations of the initial substances given in Table 1. The simple copper and zinc salts in solution totaled 0.05 mole for each. The results of our measurements are given in Table 2. We see from the Table that the difference between the reversible electrode potentials of copper and zinc in solutions of complex salts is less than in solutions of simple salts. The p.d. between the reversible electrode potentials drops from 1.1 to 0.457 volt in the transition from solutions of copper and zinc sulfates to solutions containing pyrophosphates, oxalates, ammonia, and cyanides. In solutions containing thiocyanates, thiosulfates, and chlorides, where the copper is present as a complex salt, with the zinc as a simple salt, the p.d. of the irreversible electrode potentials ranges from 0.500 to 0.977 volt.

TABLE 2

Difference Between the Reversible Electrode Potentials of Copper and Zinc in Solutions of Salts of These Metals, as a Function of the Compounds Employed (18°C)

No.	Formula of the copper or zinc compound	Reversible electrode potential, volts		P.D., volts
		copper	zinc	
1	$CuSO_4$	+0.285	-0.815	1.100
	$ZnSO_4$			
2	$Na_6Cu(P_2O_7)_2$	+0.082	-0.972	1.054
	$Na_6Zn(P_2O_7)_2$			
3	$Na_2Cu(C_2O_4)_2$	+0.093	-0.915	1.008
	$Na_4Zn(C_2O_4)_3$			
4	$Cu(NH_3)_4SO_4$.	-0.080	-1.036	0.956
	$Zn(NH_3)_4SO_4$.			
5	$Na_2Cu(CN)_3$..	-0.620	-1.077	0.457
	$Na_2Zn(CN)_4$..			
6	K_2CuCl_3.....	+0.162	-0.815	0.977
	$ZnSO_4$.....			
7	$Na_3Cu(S_2O_3)_2$	-0.120	-0.815	0.695
	$ZnSO_4$.....			
8	$KCu(CNS)_2$ ..	-0.315	-0.815	0.500
	$ZnSO_4$			

The figures enumerated in Table 2 indicate that in noncyanide solutions, as in cyanides, the reversible electrode potentials of copper and zinc can be brought much closer together by the formation of coordination compounds.

3. Cathodic polarization of copper and zinc during their deposition from solutions of complex salts. We made a study of the complexes listed in Table 1 in order to learn the effect of the cathodic polarization of copper and zinc upon the rapprochement between the deposition potentials of these metals when deposited from complex salt solutions. The results of these researches have been described at length earlier. In the present paper we shall cite merely the results of our investigations of the most typical solutions. The concentration of the initial substances in the solutions and the formulas of the complex salts are listed in Table 3. If we denote the reversible electrode potential of the metal by E_0 and the deposition potential by E_d, then the difference between the deposition potential and the reversible electrode potential will

TABLE 3

Concentration of Initial Substances in Tested Solutions and Formulas of Coordination Compounds of Copper and Zinc

No.	Solutions of Copper Salts			Solutions of zinc salts		
	Initial substances	Conc., moles per liter	Formulas of coordination compounds	Initial substances	Conc., moles per liter	Formulas of coordination compounds
1	$CuSO_4 \cdot 5H_2O$ $Na_4P_2O_7 \cdot 10H_2O$	12.5 44.6	$Na_6Cu(P_2O_7)_2$	$ZnSO_4 \cdot 7H_2O$ $Na_4P_2O_7 \cdot 10H_2O$	14.3 44.6	$Na_6Zn(P_2O_7)_2$
2	$CuSO_4 \cdot 5H_2O$ Na_2CO_3 NH_4OH (25%)	12.5 10.0 50.0	$Cu(NH_3)_4(OH)_2$	$ZnSO_4 \cdot 7H_2O$ Na_2CO_3 NH_4OH (25%)	14.3 10.0 50.0	$Zn(NH_3)_4(OH)_2$
3	$CuSO_4 \cdot 5H_2O$ $Na_2C_2O_4$	2.5 25.0	$Na_2Cu(C_2O_4)_2$	$ZnSO_4 \cdot 7H_2O$ $Na_2C_2O_4$	4.5 25.0	$Na_4Zn(C_2O_4)_3$
4	$CuSO_4 \cdot 5H_2O$ Na_2SO_3 Na_2CO_3 NaCN	12.5 10.0 10.0 8.5	$Na_2Cu(CN)_3$	$ZnSO_4 \cdot 7H_2O$ Na_2CO_3 NaCN	14.3 10.0 10.0	$Na_2Zn(CN)_4$
5	$CuSO_4 \cdot 5H_2O$ $C_3H_8O_3$ (glycerin) NaOH	12.5 10.0 100.0	$NaCu(C_3H_5O_3)$	$ZnSO_4 \cdot 7H_2O$ NaOH	14.3 100.0	$Na_2Zn(OH)_4$

be the cathodic polarization of this metal, ΔE, viz.:

$$E_d^c - E_0 = \Delta E. \qquad (4)$$

In the electrolysis of the solutions listed in Table 3, the cathode potential of copper becomes more highly electronegative than does the cathode potential of zinc as the C.D. is raised. This causes the deposition potentials of the two metals to come closer together, as is readily seen in the polarization curves of Figs. 1 and 2.

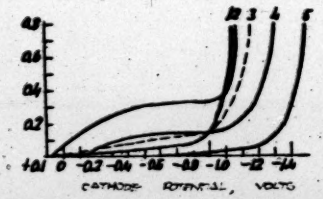

Fig. 1. Curves of the decomposition of copper from the following solutions: 1) $Na_2Cu(C_2O_4)_2$ (0.01 molar); 2) $Cu(NH_3)_4(OH)_2$ (0.05 molar); 3) $Na_6Cu(P_2O_7)_2$ (0.05 molar); 4) $NaCu(C_3H_5O_3)$ (0.05 molar); 5) $Na_2Cu(CN)_3$ (0.05 molar).

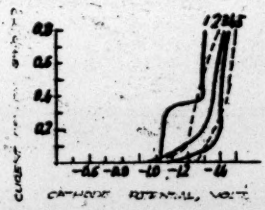

Fig. 2. Curves of the deposition of zinc from the following solutions: 1) $Zn(NH_3)_4(OH)_2$ (0.05 molar); 2) $Na_4Zn(C_2O_4)_3$ (0.01 molar); 3) $Na_6Zn(P_2O_7)_2$ (0.05 molar); 4) $Na_2Zn(CN)_4$ (0.05 molar); 5) $Na_2Zn(OH)_4$ (0.05 molar).

This is mainly due to the low concentration of simple copper ions, compared to that of the simple ions of zinc, in the solutions of the corresponding complex salts, since the instability constants of copper coordination compounds (Table 1) are much smaller than the instability constants of the zinc compounds in solutions containing the same coordinated group. The values of cathodic polarization of copper and zinc at a C.D. of 0.5 amp per sq. dm are listed in Table 4. We see from this table that the cathodic polarization (overvoltage) of copper in various solutions of its coordination compounds ranges from 0.828 to 1.184 volts, while the zinc overvoltage does not exceed 0.420 volt.

TABLE 4

Cathodic Polarization of Copper and Zinc in the Electrolysis of Their Complex Salt Solutions. C.D. = 0.5 Amp/Sq.Dm; Solution Temperature: 18-20°

No.	Formulas of complex salts of copper and zinc	Reversible electrode potential, E_o, volts	Deposition potential, E_d, volts	Cathodic polarization, $E_d - E_o = \Delta E$, volts
1	$Na_6Cu(P_2O_7)_2$	+0.082	-1.102	1.184
2	$Cu(NH_3)_4(OH)_2$	+0.051	-1.042	1.093
3	$Na_2Cu(C_2O_4)_2$	+0.044	-1.016	1.060
4	$NaCu(C_3H_5O_3)$	-0.125	-1.262	1.137
5	$Na_2Cu(CN)_3$	-0.620	-1.448	0.828
6	$Na_6Zn(P_2O_7)_2$	-0.972	-1.392	0.420
7	$Zn(NH_3O_4(OH)_2$	-1.040	-1.305	0.265
8	$Na_4Zn(C_2O_4)_3$	-0.926	-1.292	0.366
9	$Na_2Zn(CN)_4$	-1.077	-1.424	0.347
10	$Na_2Zn(OH)_4$	-1.255	-1.473	0.218

4. Simultaneous deposition of copper and zinc at the cathode from solutions of complex salts.

The simultaneous cathodic deposition of copper and zinc from solutions of mixtures of copper and zinc salts requires that their deposition potentials be alike. In solutions of their simple salts where the difference between the normal potentials of copper and zinc is 1.1 volts, the deposition potentials of these metals cannot be brought close enough together. The deposition potentials of copper and zinc are brought close together during the electrolysis of solutions of their complex salts as the result of the differences in the increases in their overvoltages.

The results of measuring the deposition potentials of copper and zinc in solutions of simple and complex salts at a cathode C.D. of 0.5 amp/sq dm are given in Table 5. The composition of these solutions is given in Table 3.

These measurements indicate that the difference between the deposition potentials of zinc and copper is 1.139 volt in solutions of their simple salts. In solutions of the noncyanide complex salts the difference between the deposition potentials of zinc and copper drops as low as 0.290-0.211 volt. In the cyanide solution and in the solutions in which copper is present as a coordination compound, while zinc is present as a simple salt, the deposition potential of zinc is more electropositive than the deposition potential of copper. As our experiments have shown, copper and zinc can be simultaneously deposited from a solution of their complex salts fairly readily at a cathode C.D. of 0.4-0.5 amp/sq dm, provided the difference between the deposition potentials of the zinc and the copper is 0.2-0.3 volt.

In the simultaneous cathodic deposition of copper and zinc, the deposition potential of the zinc is shifted toward the electropositive, approaching the value of the deposition potential of copper, as the result of the energy of formation of the copper-zinc solid solution. The polarization curves of Fig. 3, plotted in the deposition of copper, zinc, and brass from solutions of pyrophos-

phate complex ions, may be cited as examples that illustrate the depolarizing effect of the energy of formation of the copper-zinc solid solution upon the deposition potential of zinc. We see from the figure that as the current density rises, the deposition potentials of copper (Curve 1) and of zinc (Curve 2) come closer together. The difference between the deposition potentials of zinc and copper drops to 0.270 volt at a cathode C.D. of 0.6 amp/sq dm.

When copper and zinc are deposited simultaneously at the cathode from a solution containing a mixture of copper and zinc complex ions, the deposition potential of brass becomes much more electropositive than the deposition potential of zinc at a C.D. of as little as 0.1 amp per sq. dm, its magnitude approaching that of the deposition potential of copper. As the C.D. rises, the deposition potential of brass becomes more electropositive than the deposition potential of copper, as is seen from the intersection of the polarization curves. This proves that the simultaneous cathodic deposition of copper and zinc involves the mutual depolarizing effect of these metals upon their deposition potentials, tending to reduce the latter. Similar polarization curves were secured when we measured the deposition potentials of copper, zinc, and brass from the solutions of the other complex salts listed in Table 5. This method, involving the use of polarization curves, was employed in the initial stage of the present research to explore the theoretical prerequisites for the cathodic deposition of brass from solutions of noncyanide complex salts of copper and zinc. In the ensuing tests, these solutions were used to secure practical cathodic copper-zinc deposits containing up to 75% of zinc.

TABLE 5

Difference Between the Deposition Potentials of Copper and Zinc in their Cathodic Deposition from Solutions of Simple and Complex Salts (Cathode C.D. = 0.5 Amp/Sq Dm; Temperature = 18-20°

No.	Formulas of copper and zinc salts	Copper deposition potential, volts	Zinc deposition potential, volts	Difference between deposition potentials, $E_{Cu} - E_{Zn}$ = = E, volts
1	$CuSO_4$ $ZnSO_4$	+0.261	-0.878	1.139
2	$Na_6Cu(P_2O_7)_2$ $Na_6Zn(P_2O_7)_2$	-1.102	-1.392	0.290
3	$Na_2Cu(C_2O_4)_2$ $Na_4Zn(C_2O_4)_3$	-1.016	-1.292	0.276
4	$Cu(NH_3)_4(OH)_2$ $Zn(NH_3)_4(OH)_2$	-1.042	-1.305	0.263
5	$NaCu(C_3H_5O_3)$ $Na_2Zn(OH)_4$	-1.262	-1.473	0.211
6	$Na_2Cu(CN)_3$ $Na_2Zn(CN)_4$	-1.448	-1.424	-
7	K_2CuCl_3 $ZnSO_4$	-1.054	-0.878	-
8	$Na_3Cu(S_2O_3)_2$ $ZnSO_4$	-1.155	-0.878	-
9	$KCu(CNS)_2$ $ZnSO_4$	-1.225	-0.878	-

Thus, this research has proved that copper and zinc can be deposited simultaneously from solutions of noncyanide complex salts just as readily as from solutions of complex cyanides.

In our study of the properties of the copper-zinc coatings deposited from

non-cyanide solutions, we found that these coatings were unsuitable for use, in most instances, as electroplating coatings. The most satisfactory coatings, as far as electroplating quality is concerned, were produced in the oxalate bath and in the alkaline bath containing glycerol.

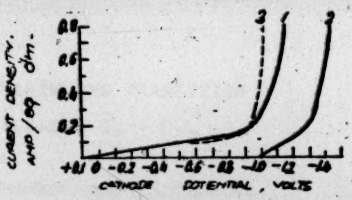

Fig. 3. Curves of the deposition potentials of copper, zinc, and brass from the following solutions.

1) $Na_6Cu(P_2O_7)_2$ (0.05 molar); 2) $Na_6Zn(P_2O_7)_2$ (0.05 molar); 3) $Na_6Cu(P_2O_7)_2$ (0.05 molar) + $Na_6Zn(P_2O_7)_2$ (0.05 molar).

SUMMARY

1 In an investigation of solutions of various complex salts of copper and zinc it has been found that the instability constants of complex copper ions are smaller than the instability constants of complex zinc ions in pyrophosphate, oxalate, and ammoniacal solutions, exactly as is the case in cyanide solutions. Therefore, the concentration of simple copper ions in these solutions decreases faster during the formation of a coordination compound than does the concentration of simple zinc ions.

2. It has been shown that in solutions containing chlorides, thiocyanates, thiosulfates, oxalates, pyrophosphates, and ammonia, the reversible electrode potentials of copper and zinc come much closer together than they do in their sulfate solutions. In the electrolysis of these solutions, as well as of alkaline solutions containing glycerol, the rapprochement of the copper and zinc deposition potentials is due to the difference in the increase of cathodic polarization of the deposited metals. At a cathodic C.D. of 0.5 amp/sq dm, the difference between the deposition potentials of copper and zinc does not exceed 0.290 volt.

2. It has been found that when a solution of a mixture of noncyanide complex salts is electrolyzed, copper and zinc are simultaneously deposited on the cathode, in most instances, at a C.D. of 0.4-0.5 amp/sq dm. Using different electrolysis conditions made it possible to achieve cathodic copper-zinc deposits in practice that contained up to 75% of zinc.

4. This research has proved that the simultaneous cathodic deposition of copper and zinc can be as readily effected at a relatively low C.D. from solutions of their noncyanide complex salts as from cyanide solutions. In most instances, however, the resulting copper-zinc deposits are unsatisfactory as electroplating coatings. The most satisfactory brass coatings, as far as electroplating quality is concerned, were secured in the oxalate bath and in the alkaline bath containing glycerol.

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THE CRYOSCOPIC CONSTANTS AND TRANSITION POINTS OF THE n-ALKANES $C_8 - C_{20}$

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In connection with a research project on the preparation of pure n-alkanes, we found it necessary to make a systematic determination of the purity of these hydrocarbons. As we know, the purity of a hydrocarbon is given by the equation:

$$N = 100 - A\,t, \qquad (1)$$

where N = the molar per cent of the principal constituent.

A = the cryoscopic constant characteristic of each hydrocarbon, in molar per cent per degree.

t = the depression of the initial freezing point of the pure hydrocarbon caused by impurities.

As we see in Equation (1), calculation of the purity of a hydrocarbon requires the precise values of the crystallization points of the pure hydrocarbon and its cryoscopic constant.

The present paper deals with the experimental determination of the cryoscopic constants of the n-alkanes. We also investigated the transition points of the n-alkanes, inasmuch as these points may be of service in determining the purity of n-alkanes.

Characteristics of the initial hydrocarbons. We prepared n-hexane by hydrogenating heptyl alcohol. We prepared n-heptane from standardized n-heptene, which was refined with sulfuric acid and then distilled into a tower with an efficiency of 33 theoretical trays under operational conditions.

The n-octane was synthesized by M.I.Rosengart.

The n-nonane was prepared by hydrogenating decyl alcohol.

The $C_{10} - C_{19}$ n-alkanes were isolated by M.D.Tilicheev and Yu.M.Kachmarchik from the hydrogenated distillate of cracking paraffin.

The n-eicosane was synthesized by N.I.Shuikin and N.A.Pozdnyak, and underwent further refining before use. The constants of these initial hydrocarbons are listed in Table 1.

Experimental procedure. The method of determining the crystallization point of n-alkanes has been described in detail in our previous paper [1].

The apparatus used to cool the tested hydrocarbons is shown in Figs. 1 and 2. The temperature was measured with a copper-constantan thermocouple, the emf being measured with a Leeds and Northrup K-2 potentiometer.

Cryoscopic constants of n-alkanes. In this research the cryoscopic constants of the C_8H_{20} n-alkanes were determined experimentally by the depression of the crystallization temperature of the tested n-alkane caused by adding 2 to 5% (molar) of other hydrocarbons. The cryoscopic constants were computed from

TABLE 1

Physicochemical Constants of Initial n-Alkanes

No.	n-Alkane	Boiling point, °	Pressure, mm	d_4^{20}, reduced to vacuum	n_D^{20}	Temperature of crystallization, °	Purity, molar %
1	n-Hexane.....	68.6-68.9	760	0.6595	1.3744	-95.45 ± 0.15	99.4 (±0.6)
2	n-Heptane ...	98.4	760	0.6834	1.3870	-90.7 ± 0.15	99.5 (±0.7)
3	n-Octane.....	124.6-124.8	760	0.7028	1.3980	-57.0 ± 0.15	99.0 (±0.7)
4	n-Nonane.....	149.4-150.2	760	0.7177	1.4060	-53.7 ± 0.15	99.4 (±0.5)
5	n-Decane.....	71.7-71.8	20	0.7315	1.4122	-30.0 ± 0.1	98.2 (±0.6)
6	n-Undecane...	76.1-76.4	10	0.7429	1.4180	-26.36 ±0.08	96.9 (±0.4)
7	n-Dodecane...	81.7-82.3	5.4	0.7503	1.4218	-10.06 ±0.08	97.2 (±0.5)
8	n-Tridecane..	82.6-83.5	3	0.7563	-	-5.35 ±0.06	99.7 (±0.3)
9	n-Tetradecane	106.3-107.3	5	0.7630	1.42888	±5.75 ±0.06	100
10	n-Pentadecane	128.0-129.7	8	0.7684	1.43184	9.81 ±0.06	99.7 (±0.3)
11	n-Hexadecane.	127.0-127.7	3	0.7735	-	18.09 ±0.06	99.8 (±0.4)
12	n-Heptadecane	153.6-153.8	7	0.7783	-	21.93 ±0.06	99.9 (±0.3)
13	n-Octadecane.	152.8-153.7	4	0.7823	-	28.10 ±0.08	100
14	n-Nonadecane.	168.6-169.3	5	0.7858	-	31.75 ±0.08	99.7 (±0.4)
15	n-Eicosane...	183.0-183.5	5	0.7889	-	36.35 ±0.10	99.9 (±0.8)

the equation:

$$A = \frac{g}{\Delta t}, \qquad (2)$$

where g = molar per cent of impurity added to the mixture.

The experimental values secured in the present research are listed in Table 2.

Whenever the heat of fusion of the tested n-alkane is known, the cryoscopic constant A may be calculated from the equation:

$$A = \frac{\lambda_f \cdot 100}{R \cdot T_f^2} \quad , \qquad (3)$$

where λ_f = the heat of fusion, in cal/mole, of the pure n-alkane at the temperature T_f.

T_f = the fusion point of the pure n-alkane, in °K.

R = the gas constant in cal/°/mole (1.98).

TABLE 2

Experimental Data on the Cryoscopic Constants of the n-Alkanes

No.	Mixture analyzed	Δt* (in °)	Depression due to addition of 1% of impurity a, (deg./%)	Cryoscopic constant A, (%/deg.)
1	n-Hexane (94.54%)** + cyclohexane (5.46%)[2]	1.20±0.02	0.220±0.005	4.5
2	n-Heptane (95.02%) + toluene (4.98%)	1.02±0.02	0.201±0.005	5.0
3	n-Heptane (95.10%) + methylcyclohexane (4.90%).....	1.00±0.02	0.201±0.005	5.0
4	n-Octane (94.02%) + n-xylene (5.98%).....	1.22±0.02	0.201±0.005	5.0
5	n-Octane (95.14%) + ethylbenzene (4.86%)....	0.97±0.02	0.250±0.005	5.0
6	n-Nonane (93.09%) + diisoamyl (3.91%).....	1.00±0.02	0.256±0.005	3.9
7	n-Decane (96.5%) + dicyclohexyl (3.5%).....	0.62±0.008	0.177±0.002	5.7
8	n-Undecane (97.60%) + dicyclohexyl (2.40%)..	0.58±0.008	0.242±0.003	4.2
9	n-Dodecane (97.79%) + dicyclohexyl (2.21%)..	0.35±0.007	0.158±0.004	6.3
10	n-Tridecane (96.26%) + dicyclohexyl (3.74%).	0.82±0.007	0.219±0.002	4.6
11	n-Tetradecane (97.42%) + dicyclohexyl (2.58%).....	0.37±0.007	0.143±0.002	7.0
12	n-Pentadecane (94.54%) + dicyclohexyl (5.46%).....	1.07±0.007	0.196±0.001	5.1
13	n-Hexadecane (96.84%) + dicyclohexyl (3.16%)	0.43±0.007	0.136±0.002	7.3
14	n-Heptadecane (94.81%) + dicyclohexyl 5.19%).....	0.96±0.007	0.185±0.001	5.4
15	n-Octadecane (97.00%) + dicyclohexyl (3.00%)	0.39±0.007	0.130±0.002	7.8
16	n-Nonadecane (92.79%) + dicyclohexyl (7.21%)	1.40±0.01	0.194±0.001	5.1
17	n-Eicosane (98.06%) + dicyclohexyl (1.94%)..	0.24±0.01	0.124±0.005	8.1

Our experimental values of the cryoscopic constants are compared in Table 3 with the values calculated from Equation (3), using the available data on the heats of fusion of these hydrocarbons.*** It is worthy of note that, with the exception of n-nonane,**** all the cryoscopic constants listed in Table 3 have been determined experimentally for the first time in the present research.

As we see in Table 3, our experimental values of the cryoscopic constants of the n-alkanes (C_8-C_{20}) are in good agreement with the values computed from

*Δt - the difference between the crystallization temperature of the initial n-alkane and that of the specified mixture

**These are molar percentages

***The values of the heats of fusion have been taken from [3,4,5].

****The cryoscopic constant of n-nonane has also been determined by Streiff and his associates [6].

Equation (3). Henceforth we shall use the experimental values of the cryoscopic constants as the most reliable ones.

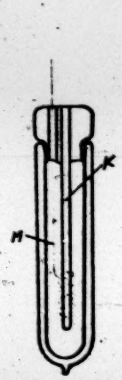
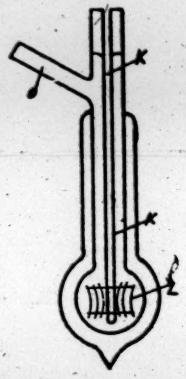


Fig. 1. Device for thermal analysis, using a cylindrical Dewar flask.



2. Spherical Dewar flask for thermal analysis

k) pocket for thermocouple; l) copper latice for flattenning out the temperature gradients; o) opening for pouring in the product.

TABLE 3

Cryoscopic Constants of the n-Alkanes

n-Alkane	Cryoscopic constant A, per cent/degree	
	Experimental	Calculated from heat of fusion
n-Pentane	–	–
n-Hexane.....	4.5	4.7
n-Heptane.....	5.0	5.0
n-Octane	5.0	5.3
n-Nonane.....	3.9	3.9
n-Decane.....	5.7	5.9
n-Undecane....	4.2	4.3
n-Dodecane....	6.3	6.4
n-Tridecane...	4.6	–
n-Tetradecane.	7	6.9
n-Pentadecane.	5.1	–
n-Hexadecane..	7.3	–
n-Heptadecane.	5.4	–
n-Octadecane..	7.8	–
n-Nonadecane..	5.1	–
n-Eicosane....	8.1	7.8

Fig. 3. shows the cryoscopic constants, found experimentally, as functions of the number of carbon atoms.

The values of the cryoscopic constants of the n-alkanes C_5-C_8 lie on a single straight line. As for the high molecular n-alkanes, they must be divided into n-alkanes with odd and even numbers of carbon atoms.

The cryoscopic constants of the n-alkanes C_{10}-C_{20} with an even number of carbon atoms lie on a prolongation of the straight line for the cryoscopic constants of the C_5-C_8 n-alkanes.

The cryoscopic constants of the n-alkanes with an odd number of carbon atoms (from C_9 to C_{17}) lie on a different straight line, somewhat below the first one. This indicates that the n-alkanes with an odd number of carbon atoms, from C_9 to C_{17}, possess a lower heat of fusion than the n-alkanes possessing an even number of carbon atoms.

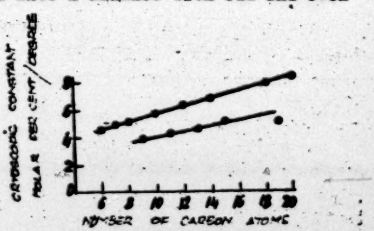


Fig. 3. Cryoscopic constants of the n-alkanes as a function of the number of carbon atoms.

The cryoscopic constant of n-$C_{18}H_{40}$ falls below the line on which the cryoscopic constants of the C_9-C_{17} n-alkanes with odd numbers of carbon atoms lie.

TABLE 4

Transition Points of the n-Alkanes

n-Alkane	Crystallization point, °	Transition point, °	Δt°, Difference between the crystallization point and the transition point, °	Transition point according to the literature, °
n-Nonane	-53.7 ±0.15	-56.6 ±0.6	2.9	-56.3 [3]
n-Undecane.....	-26.36±0.08	-36.7 ±0.3	10.3	-37.0 [4]
n-Tridecane ...	- 5.35±0.06	-18.30±0.08	12.95	–
n-Pentadecane..	9.81 ±0.06	- 2.86±0.06	12.67	-3.86 [3]
n-Heptadecane..	21.93±0.06	10.52±0.06	11.41	10 [2]
n-Nonadecane...	31.75±0.08	21.75±0.08	10.00	–

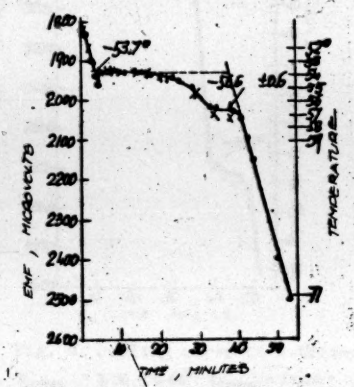


Fig. 4. Cooling curve of n-nonane.

- - - Lower thermocouple junction
X X X Upper thermocouple junction.

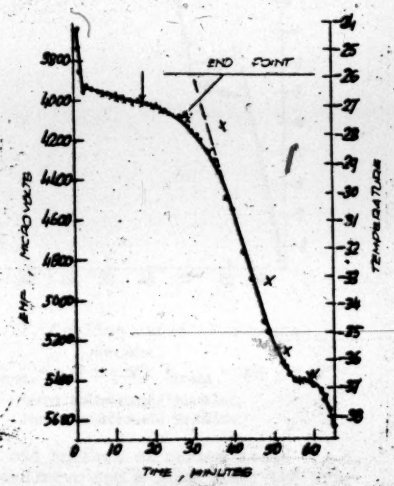


Fig. 5. Cooling curve of n-undecane.

$t_{cryst.} = -26.36 \pm 0.08°$; $t_{trans.} = -36.7 \pm 0.3°$.

- - - Lower thermocouple junction
X X X Upper thermocouple junction.

This must be attributed to the fact that transitions within the solid phase are observed for the n-alkanes with an odd number of carbon atoms (upward of C_9).

In the present research we plotted cooling curves for all the n-alkanes, from C_9 to C_{20}; only for the n-alkanes with an odd number of carbon atoms did we find any transitions occurring in the solid phase (Figs. 4-9). The transition points are listed in Table 4.

As Parks and Hoffman [3] have shown, the sum total of the heats of fusion and transition vary but little, when expressed in calories per gram, for hydrocarbons of similar structure. Therefore, whenever an n-alkane has a transition point in the solid phase, its heat of fusion will be diminished by about the amount corresponding to the heat of transition in the solid phase. This makes it clear why the n-alkanes with an odd number of carbon atoms (from C_9 to C_{17}) should have a lower heat of fusion and, hence, a lower cryoscopic constant.

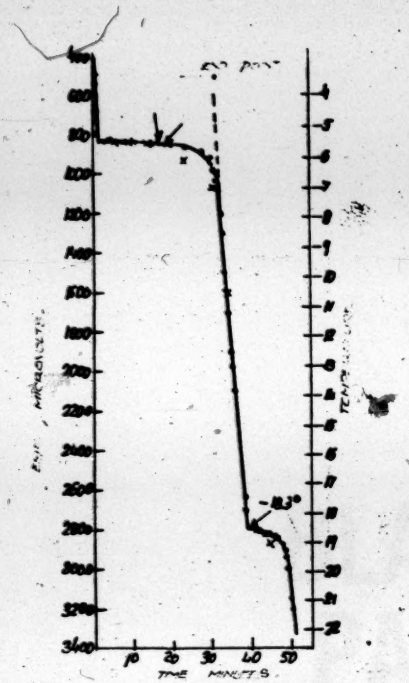


Fig. 6. Cooling curve of n-tridecane $t_{cryst.} = 5.35 \pm 0.06^{\circ}$; $t_{trans.} = 18.30 \pm 0.06^{\circ}$.

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Upper thermocouple junction

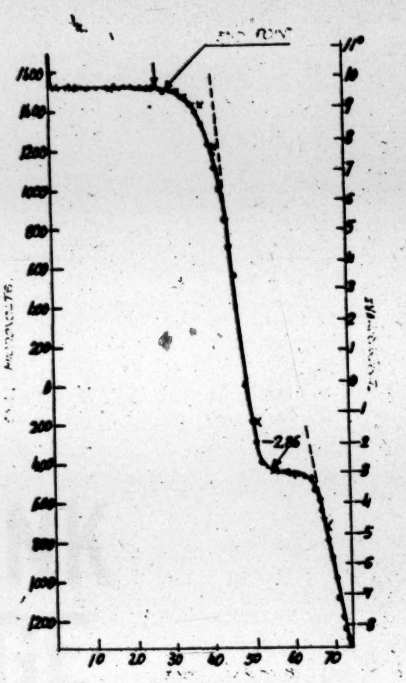

Fig. 7. Cooling curve of n-pentadecane. $t_{cryst.} = 9.81 \pm 0.06^{\circ}$; $t_{trans} = 10.5 \pm 0.06^{\circ}$

--- Lower thermocouple junction;
Upper thermocouple junction.

The difference in behavior of n-alkanes with odd numbers of carbon atoms (C_9-C_{17}) may be compared with a phenomenon that has been known for a long time; the crystallization points of n-alkanes with odd and even numbers of carbon atoms lie on two different straight lines. The value of the cryoscopic constant of n-$C_{19}H_{40}$ does not lie on the lower line contrary to expectations, but is somewhat below it. This leads us to assume that this n-alkane possesses a higher heat of transition that the other n-alkanes (from C_9 to C_{17}) with an odd number of carbon atoms, or else that this n-alkane has more than one transition point.

The behavior pattern we have found to hold good for the n-alkanes (from C_9 to C_{20}) with odd and even numbers of carbon atoms cannot be extrapolated to the higher n-alkanes. This is proved by: 1) the deviation of the cryoscopic constant for n-$C_{18}H_{40}$ from the straight line in which all the n-alkanes from C_9 to C_{17} with an odd number of carbon atoms lie; and 2) by the existence of transition points in the solid phase in the high-molecular n-alkanes with an even number of carbon atoms, such as n-C_{26}-H_{54} – n-$C_{34}H_{70}$ [5]

The reason for the difference in the behavior of the n-alkanes (C_9-C_{20}) with odd and even numbers of carbon atoms is unclear, reminding one of cis- and trans-isomerism.

While determining the heat of fusion of n-nonane, Parks and Hoffman [3] found a transition point in the solid phase at a temperature 2.4° below the initial crystallization temperature of n-nonane. These authors determined the aggregate heat of transition (the heat of the fusion plus the heat of transition), inasmuch as the phase transition occurred at a temperature close to the crystallization point. This aggregate

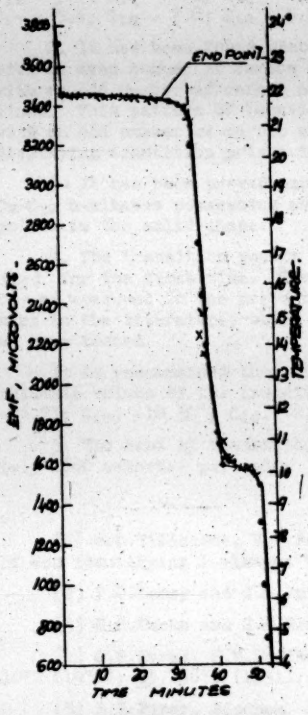

Fig. 8. Cooling curve of n-heptadecane.

$t_{cryst.}$ = 21.88 ± 0.06°; $t_{trans.}$ = = 10.5 ± 0.06°.

--- Lower thermocouple junction

××× Upper thermocouple junction.

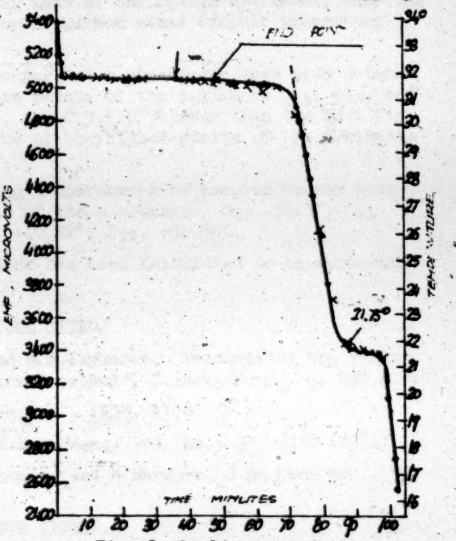

Fig. 9. Cooling curve of n-nonadecane.

$t_{cryst.}$ = 31.75 ± 0.08°; t_{trans} = 21.75 ± 0.08°.

--- Lower thermocouple junction

××× Upper thermocouple junction.

heat totaled 5,280 calories per mole. From this we computed the heat of transition of n-nonane as follows:

$$Y_{trans.} = 5280 - 3660 = 1620 \text{ cal/mole, or roughly } 1600 \text{ cal/mole.}$$

The values of the cryoscopic constants as measured in the present research and the available data on the crystallization points of the n-alkanes make it possible to calculate the purity of the n-alkanes from C_5 to C_{20} from their initial crystallization points.

SUMMARY

1. The following cryoscopic constants have been found for the n-alkanes C_6-C_{20}, in molar per cent per degree: C_6 - 4.5; C_7 - 5.0; C_8 - 5.2; C_9 - 3.9; C_{10} - 5.7; C_{11} - 4.2; C_{12} - 6.3; C_{13} - 4.6; C_{14} - 7.0; C_{15} - 5.1; C_{16} - 7.3; C_{17} - 5.4; C_{18} - 7.8; C_{19} - 5.1; C_{20} - 8.1.

2. It has been found that the cryosccpic constants of the n-alkanes C_6-C_{20} with an even number of carbon atoms, on the one hand, and of the n-alkanes C_9-C_{17}, with an odd number of carbon atoms, on the other, lie on two different straight lines. This pattern of behavior is due to the fact that the C_9-C_{17} n-alkanes, with an odd number of carbon atoms, have lower heats of fusion, owing to their displaying transition points in the solid phase.

3. It has been proved experimentally that of the C_6-C_{20} n-alkanes, only the C_9-C_{19} n-alkanes possessing an odd number of carbon atoms exhibit transition points in the solid phase.

4. The transition points of n-tridecane and n-nonadecane have been determined for the first time. The transition points of the n-alkanes C_{11}, C_{15}, and C_{17} as measured in the present research, are 0.3-1.0° higher than the best figures in the literature, which is evidence of the higher purity of the n-alkanes we have tested.

It is recommended that the following temperatures be adopted as the most reliable values of the transition points of the n-alkanes: C_9, -56.3°; C_{11}, -36.7°; C_{13}, -18.30°; C_{15}, -2.86°; C_{17}, +10.52°; C_{19}, +21.75°.

5. The heat of transition of n-nonane has been calculated to be approximately 1600 calories per mole.

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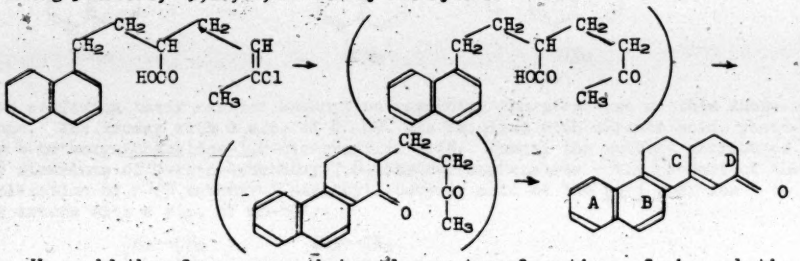
SYNTHESIS OF POLYCYCLIC HYDROAROMATIC KETONES

V. 3-KETO-7-METHOXY-1, 2, 3, 11, 12, 12a-HEXAHYDROCHRYSENE

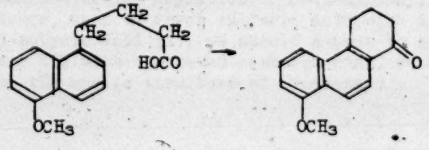
G. T. Tatevosyan and S. A. Vardanyan

In Report III [1] we showed that reacting concentrated sulfuric acid with α-(3-chlorocrotyl)-γ-(1-naphthyl)-butyric acid hydrolyzes the latter at the chlorine atom attached to a double bond, and then cyclizes it doubly, finally yielding 3-keto-1,2-3,11,12,12a-hexahydrochrysene:



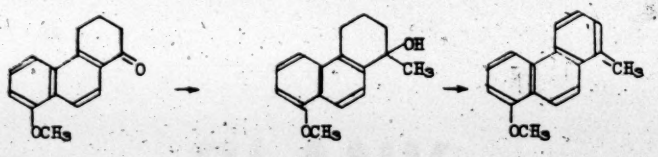
We could therefore assume that analogous transformations of ring-substituted α-(3-chlorocrotyl)-γ-(1-naphthyl)-butyric acids would yield the corresponding derivatives of 3-ketohexahydrochrysene, with substituents in the A and B rings. But since the closing of the C ring entails the intramolecular acylation of the substituted γ-(1-naphthyl)-butyric acid, the general applicability of this method of synthesis might be limited to the action of those substituents that often govern the course of cyclization. Some indications of the possible effect of various substituents upon the cyclization of α-(3-chlorocrotyl)-γ-(1-naphthyl)-butyric acids may be secured by considering the available information on the simpler instances involving the formation of tricyclic ketones by the intramolecular acylation of γ-(1-naphthyl)-butyric acids. The literature contains some information on the orienting effect of the methoxy group located at the 5 position in the naphthalene ring.

Kon and Ruzicka [2] have found that reacting stannic chloride with γ-(5 methoxy-1-naphthyl)-butyric acid yields a methoxy ketone that fuses at 137°; they assigned it the structure of 1-keto-8-methoxy-1,2,3,4-tetrahydrophenanthrene:

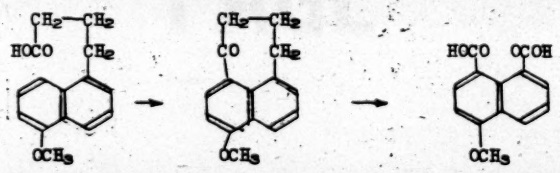


When the acid chloride of the same acid was cyclized with aluminum chloride, they got a compound with the same composition as the tricyclic methoxy ketone, but with a m.p. of 88-89°. The structure of this isomeric compound was not determined. Hill, Short, and Stromberg [3], on the other hand, have shown that reacting stannic chloride with γ-(5-methoxy-1-naphthyl)-butyric acid yields a compound with a m.p. of 88-89°. It was synthesized, with an even higher yield, by reacting a benzene solution of the acid with phosphoric anhydride. In neither instance was a compound with a m.p. of 137° formed. In view of the fact that the substance with a m.p. of 88-89° yielded a semicarbazone and a dinitrophenylhydrazone, that is, was a ketone, Hill, Short, and Stromberg concluded that it was the normal cyclization product of γ-(5-methoxy-1-naphthyl)-butyric acid – 1-keto-8-methoxy-1,2,3,4-tetrahydrophenanthrene.

In a subsequent paper Kon and Soper [4] determined the structure of both of these isomeric products. They reacted the methoxy ketone with a m.p. of 137° with methylmagnesium iodide and dehydrogenated the reaction product with palladium on charcoal, securing 1-methyl-8-methoxyphenanthrene:

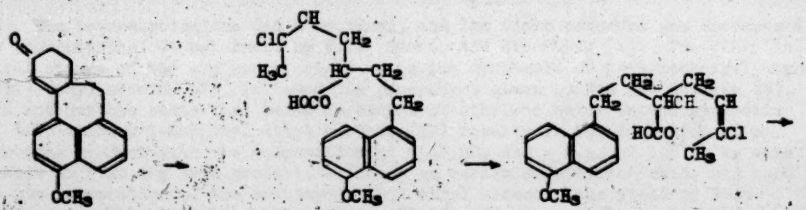


thus confiming their earlier assumption regarding the structure of this substance. The isomer with a m.p. of 88-89° was oxidized with chromic acid, yielding 4-methoxynaphthalene-1,8-dicarboxylic acid. Hence, the authors attributed the structure of 7-keto-4-methoxy-7,8-dihydrohomophenalene – the product of the cyclization of γ-(5-methoxy-1-naphthyl)-butyric acid at the <u>peri</u> position – to the ketone with a m.p. of 88-89°:

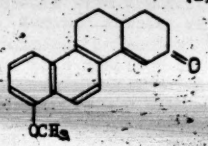


Kon and Soper likewise confirmed the observation of Hill, Short, and Stromberg, who stated that the substance with a m.p. of 88-89°, i.e., 7-keto-4-methoxy-7,8-dihydrohomophenalene, was the principal product of the cyclization of γ-(5-methoxy-1-naphthyl)-butyric acid. The methoxy ketone that has a m.p. of 137°, i.e., 1-keto-8-methoxy-1,2,3,4-tetrahydrophenanthrene, is not always synthesized, apparently, though the authors did not go into the conditions that favor its formation.

Thus, the presence of the methoxy group in the 5 position of the naphthalene ring promotes the intramolecular acylation of γ-(1-naphthyl)-butyric acids at the <u>peri</u> position. Hence, when we react sulfuric acid with α-(3-chlorocrotyl)-γ-(5-methoxy-1-naphthyl)-butyric acid (I), we should expect to get the isomeric tetracyclic methoxy ketone (III) with one seven-membered ring, rather than the methoxy ketone (II), with the cyclic structure of chrysene:



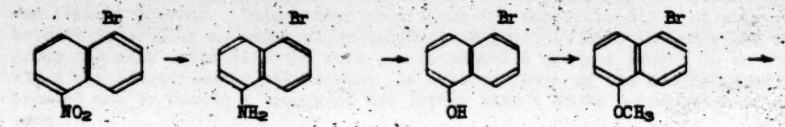
(III) (I)

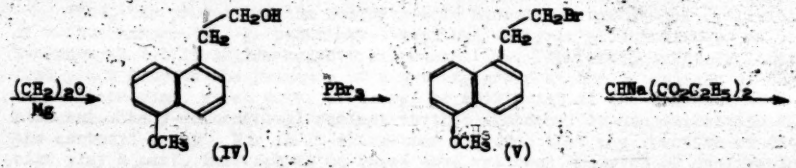


(II)

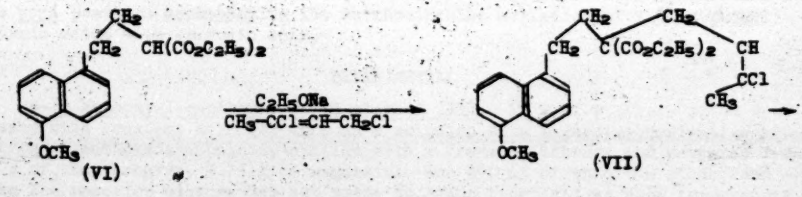
The results of this sulfuric-acid hydrolysis and of the double cyclization of the specified acid are set forth in the present report.

α-(3-Chlorocrotyl)-γ-(5-methoxy-1-naphthyl)-butyric acid was synthesized from 1-bromo-5-nitronaphthalene as follows:

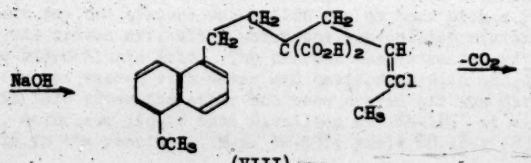




(IV) (V)



(VI) (VII)



(VIII) (I)

The bromonaphthalene was diazotized, and the diazo compound was decomposed to bromonaphthol as set forth by Hill, Short, and Stromberg [3]. The other initial stages of the synthesis, right up to the synthesis of β-(5-methoxy-1-naphthyl) ethyl bromide (V), followed the procedures given by Kon and Ruzicka [2]. Kon and Ruzicka state that using an excess of ethylene oxide in the synthesis of β-(5-methoxy-1-naphthyl ethyl alcohol (IV) results in the formation of an abnormal product with the composition of $C_{13}H_{10}O_5$ and a m.p. of 128°. We were unable to find any such product, although an excess of ethylene oxide was used in the preparation of the methoxynaphthyl ethyl alcohol, the yield of β-(5-methoxy-1-naphthyl) ethyl alcohol being 83.3%. We secured the methoxybromide (V) as a crystalline substance with a m.p. of 37-38°, though Kon and Ruzicka describe it as a liquid. Kon and Ruzicka condensed the methoxybromide with malonic ester in xylene containing "molecular" potassium. We discovered that the yield is satisfactory when this reaction is carried out with an alcoholic solution of sodium alcoholate. An alcoholic solution of sodium alcoholate was also used to condense 1,3-dichlorobutene-2 with a substituted malonic ester (VI).

We were unable to secure the acid (I) in an analytically pure state, since we could not crystallize or distil it. It was therefore subjected to sulfuric acid hydrolysis and cyclization immediately after it had been synthesized by decarboxylation of the disubstituted malonic ester (VIII), without purification. The crystalline reaction product, with a yield of 32.5% and satisfying the formulas (II) and (III) as far as its composition was concerned, formed a dinitrophenylhydrazone with 2,4-dinitrophenylhydrazine. The ketone's structure was established by dehydrogenating it at 300-320° over palladium on charcoal witout any solvent present. Under these conditions the dehydrogenation of polycyclic ketones is usually accompanied by dehydration [5]. In this instance the methoxy group was also split off; the sole dehydrogenation product proved to be chrysene, which was identified by determining the melting point of the dehydrogenation product and by fusing a sample of the latter with a known preparation of chrysene.

Thus, the product of the sulfuric-acid hydrolysis and double cyclization of α-(3-chlorocrotyl)-γ-(5-methoxy-1-naphthyl)-butyric acid proved to be 3-keto-7-methoxy-1,2,3,11,12,12a-hexahydrochrysene (II). The usual ortho cyclization took place despite the presence of a methoxy group at the 5 position of the naphthalene ring, which must, it seems, be attributed to the presence of a substituent, the 3-chlorocrotyl radical in this instance, in the α-position to the carboxyl group. Nor is it altogether excluded that the reaction conditions also play a part, inasmuch as no cases have yet been observed of cyclization at the peri position accompanying the intramolecular acylation of γ-(1-naphthyl)-butyric acids with sulfuric acid.

EXPERIMENTAL

β-(5-Methoxy-1-naphthyl) ethyl alcohol (IV). 20 g of ethylene oxide was passed with constant stirring through a solution of a magnesium derivative of 1-bromo-5-methoxynaphthalene, chilled with a freezing mixture and prepared from 96 g of that bromide, 9.21 g of magnesium, and 390 ml of absolute ether, and then the reaction mixture was set aside to stand overnight at room temperature. The next day the mixture was boiled for an hour with a reflux condenser, and the ether was driven off, after which the ice-chilled mixture was decomposed with dilute hydrochloric acid. The product was extracted with ether, and the ether solution was washed with water and desiccated with anhydrous sodium sulfate. The oil left after the ether had been driven off was distilled in vacuum. The thick, colorless liquid that distilled at 184-187° at 4-5 mm crystallized completely in the receiver. M.p. 52-53°; yield 68.18 g (83.3% of the theoretical).

β-(5-Methoxy-1-naphthyl)-ethyl bromide (V). A solution of 45.7 g of phosphorus tribromide in 236 ml of benzene was added, with constant stirring, to a water-cooled solution of 68.15 g of the alcohol (IV) in 420 ml of benzene. After the reaction mixture had been heated to 60-65° for 2 hours, it was cooled and poured over ice; the benzene solution was decanted from the acidic aqueous layer, washed with a dilute solution of sodium hydroxide and then with water, and desiccated with sodium sulfate. After the benzene had been driven off, the product was distilled at 174-176° and 3 mm. According to Kon and Ruzicka [2], β-(5-methoxy-1-naphthyl)-ethyl bromide boils at 186° and 1.7 mm. The distillate crystallized completely in the receiver. This yielded 37.9 g (42.37% of the theoretical) of a colorless crystalline substance with a m.p. of 37-38°.

0.1124 g substance: 0.0790 g AgBr. 0.1126 g substance: 0.0804 g AgBr.
Found %: Br 29.90, 30.39. $C_{13}H_{13}OBr$. Computed %: Br 30.18.

β-(5-Methoxy-1-naphthyl)-ethyl malonate (VI). 37.4 g of the bromide (V) was added, with chilling and constant stirring, to a solution of sodium malonic ester, prepared from 37 g of malonic ester, 3.41 g of sodium, and 34.5 g of absolute alcohol. The mixture was boiled for 4 hours with a reflux condenser. Then [illegible] precipitate of sodium bromide dissolving completely), the oily reaction product was dissolved in ether, and the ether solution was washed with water and desiccated with sodium sulfate. After the ether had been driven off, the product distilled at 206-208° and 9 mm. This yielded 31.6 g (65% of the theoretical) of the β-(5-methoxy-1-naphthyl)-ethyl malonate previously described by Kon and Ruzicka, as a viscous, colorless liquid.

β-(5-methoxy-1-naphthyl)-ethyl-(3-chlorocrotyl)-malonate (VII). 31.6 g of the ester (VI) was added to a solution of sodium alcoholate, prepared from 2.25 g of sodium and 30 g of absolute alcohol. The solution was allowed to stand for half an hour at room temperature, and then 15 g of freshly distilled 1,3-dichlorobutene-2 was added gradually to the water-cooled and stirred solution. The mixture was boiled for 6 hours, after which it was cooled, and dilute hydrochloric acid was added until all the precipitated sodium chloride dissolved. The product was then extracted with ether. Washing the ether solution with water caused a crystalline substance to settle out. The solution was poured into a crystallizing pan. Driving off the ether yielded 30.42 g (76.5% of the theoretical) of the crude crystalline product. Recrystallization from alcohol yielded the disubstituted malonic ester (VII) as colorless needles with a m.p. of 69-70°.

0.1100 g substance: 0.0370 g AgCl. 0.1139 g substance: 0.0390 g AgCl.
Found %: Cl 8.32, 8.47. $C_{24}H_{29}O_5Cl$. Computed %: Cl 8.21.

β-(5-Methoxy-1-naphthyl)-ethyl-(3-chlorocrotyl)-malonic acid (VIII). A mixture of 30 g of the crude ester (VII), 7.6 g of sodium hydroxide, and 114 g of 95% alcohol was boiled for 5 hours with a reflux condenser. After the mixture had cooled, 200 ml of water was added, and the alcohol was driven off. The thick oil that separated out when the chilled mixture was acidulated with dilute hydrochloric acid crystallized completely when rubbed with a glass rod. The crystals were filtered out of the mother liquor, washed with water, dried at room temperature, and recrystallized from 50% alcohol. This yielded 22.6 g (86.6% of the theoretical) of a colorless, finely crystalline powder, with a m.p. of 167-168°.

0.1078 g substance: 0.0391 g AgCl. 0.1034 g substance: 0.0394 g AgCl.
Found %: Cl 9.36, 9.43. $C_{20}H_{21}O_5Cl$. Computed %: Cl 9.42.

3-Keto-7-methoxy-1,2,3,11,12,12a-hexahydrochrysene (II). As indicated above, the α-(3-chlorocrotyl)-γ-(5-methoxy-1-naphthyl)-butyric acid was reacted with sulfuric acid as soon as it was prepared by decarboxylating the dibasic acid

(VIII). When decarboxylated at reduced pressure (water-jet pump), the acid (I) is secured as a faintly colored, very tacky mass, all of which sticks to the walls of the container as it cools. 2.5 g of the dibasic acid (VIII) was decarboxylated at reduced pressure by heating it over an open flame. After no more carbon dioxide was evolved, and the decarboxylation product had cooled to room temperature, to 60 ml sulfuric acid, sp. gr. 1.78, was added. Frequent agitation of the small flask gradually gradually caused all the acid (I) to dissolve in the sulfuric acid; this took about one hour. The dissolution of the acid (I) entailed the evolution of hydrogen chloride. Then the reaction mixture was heated for an hour to 60-65° in a current of carbon dioxide over a water bath, and left to stand overnight. The next day the flask contents were poured over ice, and the resultant crystalline substance was dissolved in a large quantity of ether; the ether solution was carefully washed with a 10% sodium hydroxide solution and then with water, desiccated with sodium sulfate, filtered, and set aside to evaporate. Nothing was recovered from the solution when the alkaline wash waters were acidulated. As the ether evaporated it left behind 0.6 g (32.5% of the theoretical) of yellowish crystals. The substance was triply crystallized from methanol (boiling with charcoal). The colorless crystals had a m.p. of 192.5-193°.

0.1173 g substance: 0.3539 g CO_2; 0.0731 g H_2O. Found %: C 82.28; H 6.89. $C_{18}H_{18}O_2$. Computed %: C 82.01; H 6.47.

The orange-yellow 2,4-dinitrophenylhydrazone, produced by heating a mixture of 0.3 g of the ketone, 0.14 g of dinitrophenylhydrazine, and 40 ml of alcohol, had a m.p. of 249-250° after recrystallization from a chloroform-alcohol mixture.

0.0704 g substance: 8.5 ml N_2 (31°, 678 mm). Found %: N 12.12. $C_{25}H_{27}O_5N_4$. Computed %: N 12.22.

Dehydrogenation. 0.2 g of the ketone was heated in nitrogen with 0.04 g of a Pd catalyst on charcoal, containing 10% of palladium. The evolution of gas set in at 190-200°, but the temperature was quickly raised to 300-320°, the dehydrogenation was continued at that temperature for one hour. The temperature was raised still higher toward the end of the run, and the dehydrogenation product began to sublime, settling on the cold walls of a quartz test tube as light leaflets that displayed bluish-violet fluorescence. Heating was stopped when no more substance sublimed. The crystals were removed, and the residue left in the test tube was processed a few times with boiling benzene, a little at a time. The benzene extract was washed with a 10% soda solution and then with water, desiccated with sodium sulfate, filtered, and set aside to evaporate. When the alkaline solution that had been used to wash the benzene extract was acidulated, a barely perceptible quantity of a flocculent acidid dehydrogenation product settled out. Driving off the benzene left a small amount of a dirty crystalline substance, which was also sublimed. A small quantity of crystals settled on the test tube walls, which looked no different from the crystals that had sublimed during dehydrogenation. Both batches of crystals fused at 252-253° (corrected). A fusion sample mixed with a known preparation of chrysene (m.p. 251-252°, corrected) exhibited no depression (m.p. 251-253°).

SUMMARY

A study has been made of the sulfuric-acid hydrolysis and double cyclization of α-(3-chlorocrotyl)-γ-(5-methoxy-1-naphthyl)-butyric acid, synthesized in a malonic synthesis from β-(5-methoxy-1-naphthyl)-ethyl bromide and 1,3-dichlorobutene-2.

It has been shown that in this instance the usual ortho cyclization takes place, yielding as its end product 3-keto-7-methoxy-1,2,3,11,12,12a-hexahydro-

chrysene, notwithstanding the presence of a methoxy group at the 5 position of the naphthalene ring, which favors the *peri* cyclization of γ-(1-naphthyl)-butyric acids according to some assertions in the literature.

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*See CB translation p. 298 ff.

THE REACTION OF VINYL IODIDE WITH MAGNESIUM

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Numerous papers have dealt with the reactions between magnesium and unsaturated halogen derivatives with the halogen atom attached to the carbon atom at the double bond, attention being focussed mainly upon the homologs of the vinyl halides. These papers indicate that most of the homologs of vinyl bromide when reacted with magnesium, form organomagnesium compounds that may be employed in subsequent syntheses (the researches of Yavorsky, Krestinsky, Tiffeneau, and others). But in some instances the reaction takes an abnormal course, either no organomagnesium compounds being secured at all or else the yields are low.

Practically no research has yet been done on the problem of the reaction of an unsubstituted vinyl halide with magnesium. Krestinsky [1] was the first to try to prepare an organomagnesium compound from magnesium and vinyl bromide for use in synthesizing unsaturated alcohols. He observed that ethylene and acetylene were evolved, though no organomagnesium compound was produced. We also possess data on the use of vinyl bromide mixed with other halogen derivatives for synthesizing unsaturated hydrocarbons, though nothing is said about the feasibility of producing an organomagnesium compound from vinyl bromide.

We made an investigation to determine the feasibility of preparing a vinylmagnesium halide and of employing this organomagnesium compound in synthesizing unsaturated alcohols. The present paper describes the results of our research on the reaction of magnesium with vinyl iodide.

When vinyl iodide is reacted with magnesium, the following processes may occur: 1. The formation of vinylmagnesium iodide. 2. The formation of acetylene and ethylene;

$$2CH_2{=}CHI + Mg \longrightarrow CH{\equiv}CH + CH_2{=}CH_2 + MgI_2.$$

We have represented this reaction as an overall equation, like the one given in the paper by V.Krestinsky [1] to explain the reaction of ω-bromostyrene with magnesium.* 3. The reaction of the acetylene with the vinylmagnesium iodide to yield diacetylenemagnesium diiodide and ethylene. 4. The formation of divinyl.

Our experiments have shown that vinyl iodide (in ether solution) reacts vigorously with magnesium. Study of the reaction products justifies the assertion that vinylmagnesium iodide is formed (Reaction 1), though acetylene and ethylene are formed at the same time (Reaction 2). Then the vinylmagnesium iodide reacts with the acetylene, yielding diacetylenemagnesium diiodide and ethylene (Reaction 3). In consequence of all these reactions, the yield of vinylmagnesium iodide is low, totaling about 5% of the theoretical (based on the vinyl iodide used for the reaction).

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*It should be noted that this paper by Krestinsky also gives another explanation of the mechanism involved in the reaction between a vinyl halide and magnesium.

When the synthesized vinylmagnesium iodide is reacted with acetone, it yields dimethylvinylcarbinol. We have synthesized this alcohol by pouring a solution of acetone in ether into the products of the reaction of vinyl iodide and magnesium. The alcohol yield was about 5% of the theoretical, based on the vinyl iodide. We also secured this alcohol by carrying out the reaction in a single stage, i.e., by adding a mixture of vinyl iodide and acetone to the magnesium. The yield of the dimethylvinylcarbinol was somewhat higher than before, totaling 7% of the theoretical.

EXPERIMENTAL

We used a round-bottomed flask, fitted with a dropping funnel and a reflux condenser, in our investigation of the reaction of vinyl iodide with magnesium. The condenser was connected to a gas tank via a calcium chloride tube. We prepared the vinyl iodide by treating ethylene iodide with sodium alcoholate [3]. It should be noted that the low yield prevented us from securing enough of the vinyl iodide, which was a great handicap in our research. In each test we used 7.7 g of vinyl iodide (0.05 mole), dissolved in 25-30 ml of absolute ether, and 1.5 g of magnesium (an excess of 25% over the quantity required theoretically).

The tests were run as follows: a small quantity of absolute ether and 2-3 drops of vinyl iodide were added to the magnesium, in the form of large chips. The reaction set in after some time had elapsed (gentle heating being used in some cases), the boiling up of the ether indicating the onset of the reaction. Then the ether solution of the vinyl iodide was added from the dropping funnel. The reaction is vigorous at room temperature, so that the vinyl iodide must be added slowly, a drop at a time, sometimes even interrupting the addition of the latter and cooling the flask with water. Adding the vinyl iodide took about 2-2.5 hours when a 0.05-molar solution was used. The gases evolved were collected in the gas tank above a saturated solution of sodium chloride. When the reaction was over, the contents of the flask were heated to 25° over a water bath for half an hour, being shaken up at intervals. Then the reaction mixture was set aside to stand, the unreacted magnesium settling out as grains or as a fine precipitate. The ether solution was drawn off into a round-bottomed flask through a siphon tube fitted with a filter. The liquid, which was cloudy at first, became transparent, an oily yellow layer settling to the bottom of the flask. After the flask had stood for a day, large colorless crystals were seen in this layer. The filtered-out magnesium was washed with ether, dried, and weighed. This gave us a rough idea of the amount of magnesium that had entered into the reaction with the vinyl chloride. More accurate figures were secured by determining the quantity of halogen in the reaction products (see below).

We found acetylene, ethylene, and divinyl in the gases evolved during the reaction. The presence of acetylene was established by the characteristic reaction involving the formation of cuprous acetylide; this was effected by passing the gas through several wash bottles filled with an ammoniacal solution of cuprous chloride. Cuprous acetylide was precipitated in the first few wash bottles, no precipitate being formed in the ensuing ones, thus proving that all the acetylene had been absorbed. The gas freed of its acetylene decolorized bromine water and reacted with an alkaline solution of permanganate. The unsaturated gaseous products present might be ethylene or divinyl, but a determination with maleic anhydride [4] indicated that the gas contained no divinyl. We therefore believe that the gas left after the acetylene had been absorbed contained ethylene.

The ether solution was treated with water after the unreacted magnesium had been filtered out. This was done in a three-necked flask, with a reflux condenser attached to one opening, a dropping funnel to another, and an inlet tube for air

to the third. The reaction was very violent, so that the water had to be added very cautiously, a drop at a time, while the flask was chilled with ice water.

The gases evolved passed through the reflux condenser into a wash bottle containing an ammoniacal solution of cuprous chloride, in which the cuprous acetylide was thrown down. From there the gas entered a wash bottle, containing a weak solution of sulfuric acid to absorb the ammonia and then passed to a graduated gasholder above a saturated solution of sodium chloride. We determined the ethylene content of the gas thus purified by measuring the absorption in bromine water in a Hempel pipet. Here, as later on, we cite the figures on a single one of these tests, inasmuch as they all yielded results that were fairly close. The aggregate volume of gas collected (ethylene + air) totaled 530 ml, of which 51 ml represented ethylene (reduced to standard conditions), equivalent to 0.35 g of vinyl iodide. Therefore the yield of vinylmagnesium iodide was about 5% of the theoretical, based on the vinyl iodide placed in reaction.

Determination of MgIOH. After the gases had been driven out of the reaction flask, the ether was driven off, and the residue was dissolved in 0.5 N nitric acid. The excess acid was back-titrated with a 0.1 N alkali solution. The amount of nitric acid totaled 52.4 ml, corresponding to 4.0 g of vinyl iodide.

Determination of halogen: the solution left after the determination of MgIOH was acidulated with nitric acid and titrated back with a 0.1 N solution of $AgNO_3$. The amount of $AgNO_3$ solution used represented 6.5 g of vinyl iodide.

The results of analysis thus indicated that about 80% of the vinyl iodide used for the reaction enters into reaction with the magnesium, of this total only 5% being used in the formation of vinylmagnesium iodide.

Synthesis of dimethylvinylcarbinol. 5.8 g of acetone (0.1 mole) in 30 ml of absolute ether was added, with chilling and constant stirring of the solution, to an organomagnesium compound prepared with 15.5 g of vinyl iodide (0.1 mole), and the reaction mixture was allowed to stand overnight. The next morning the contents of the flask were decomposed with ice water, the ether layer decanted, and the residue was extracted several times with ether. The ether extracts were desiccated with fused potash and then with barium oxide. Driving off the ether yielded a transparent yellow liquid (3-4 g). Fractionation of 3 g of this liquid (we cite the results of one of our tests), yielded the following fractions: Fraction 1, 40-80°, 0.4 g; Fraction 2, 80-110°, 0.9 g; Fraction 3, 110-180°, 0.6 g (decomposition sets in); and a residue of 0.9 g left in the flask (a brownish liquid).

Refractionation of Fraction 2: up to 95°, a few drops; 95-99° - 0.5 g of a transparent, mobile liquid with a distinctive odor.

Dimethylvinylcarbinol had been previously synthesized by Mokievsky [5], who gave its boiling point as 97-99°.

We did not investigate the higher-boiling fractions, though we believe they may contain products of the reaction of the acetone with the diacetylenemagnesium diiodide, inasmuch as all the necessary conditions for this latter reaction are present [6].

Synthesis of dimethylvinylcarbinol in a single stage. We made use of the method elaborated by Yavorsky [7] for producing allyl alcohols in effecting this synthesis. A mixture of 15.5 g of vinyl iodide (0.1 mole) and 5.8 g of acetone (0.1 mole) in 30 ml of absolute ether was poured over magnesium in ribbon form that had been previously pickled with vinyl iodide. The reaction was calm,

slowing down after only about half of the mixture had been added, as the magnesium evidently became coated with a liquid coordination compound. To ensure that the reaction is uniform, it is advisable to add the magnesium a little at a time. After all the mixture had been added to the flask, a few more coils of fresh magnesium ribbon were thrown in, and the reaction mixture was set aside to stand overnight. The remainder of the processing and the recovery of the product were the same as in the preceding experiment. The yield of the dimethylvinylcarbinol was somewhat higher than when the reaction was run in two stages, totaling 7 to 10% of the theoretical.

SUMMARY

1. The reaction of vinyl iodide with magnesium has been investigated for the first time, it being found that vinylmagnesium iodide can be produced from vinyl iodide and magnesium in absolute ether. The yield of the vinylmagnesium iodide was 5% of the theoretical.

2. It has been found that this reaction is paralleled by the formation of acetylene and ethylene and by the reaction of the vinylmagnesium iodide with the acetylene.

3. The resultant vinylmagnesium iodide can react with acetone to form dimethylvinylcarbinol, the yield being as much as 5% of the theoretical. This latter alcohol may also be synthesized in a single stage, that is, by adding a mixture of vinyl iodide and acetone to the magnesium. This raises the yield of the alcohol to 7 to 10% of the theoretical.

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THE REACTIONS OF DIMETHYLACETENYLCARBINOL WITH ETHYLENE OXIDE. I

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No one has done any research up to now on the reaction of dimethylacetenylcarbinol with alkylene oxides. This reaction may follow either one of two courses: either with the hydroxyl group of the dimethylacetenylcarbinol, yielding β-hydroxy alkyl ethers, or with the active hydrogen of the acetylene bond, yielding the corresponding glycols. The present research had as its objective the synthesis of the β-hydroxy ethyl ether of dimethylacetenylcarbinol, containing a more reactive primary alcohol group that the initial dimethylacetenylcarbinol. A study of this reaction was of even greater interest, inasmuch as we were unable to find any reference in the literature to the condensation of tertiary acetylene alcohols with alkylene oxides, with the sole exception of the paper by Nazarov and Romanov on the condensation of ethylene oxide with dimethylvinylethynylcarbinol in the presence of potassium hydroxide [1]. Under these reaction conditions Nazarov and Romanov secured a mixture of mono-, di-, and polyglycol ethers of dimethylvinylethynylcarbinol.

We used tertiary organic bases as catalysts for the condensation of dimethylacetenylcarbinol with ethylene oxide. Of these bases, dimethylaniline has been studied in detail. The use of tertiary organic bases as catalysts for the condensation of ethylene oxide with alcohols is mentioned in several patents [2,3], and in the paper by Dolgopolov, Melnikov, and Nametkin [4], who investigated the condensation of ethyl alcohol with ethylene oxide and found that tertiary organic bases orient this reaction mainly toward the formation of a monoglycol ether. This also occurred in our tests.

We synthesized the β-hydroxy ethyl ether of dimethylacetenylcarbinol by heating dimethylacetenylcarbinol, ethylene oxide, and dimethylaniline together in an autoclave [5]. The reaction is given by the following equation:

The tests we ran established that the best yields (over 70%) of the β-hydroxy ethyl ether of dimethylacetenylcarbinol were secured when the molar ratio of the alcohol to the ethylene oxide was 3:1, with the catalyst representing 4% of the initial carbinol. In contrast to dimethylacetenylcarbinol, the β-hydroxy ethyl ether of dimethylacetenylcarbinol is unaffected by alkalies and insoluble in water, so that it does not form a precipitate when reacted with ammoniacal silver nitrate. It distills at normal pressure with no signs of decomposition; it enters readily into reaction with anhydrides and acids, yielding esters. The structure of the β-hydroxy ethyl ether of dimethylacetenylcarbinol

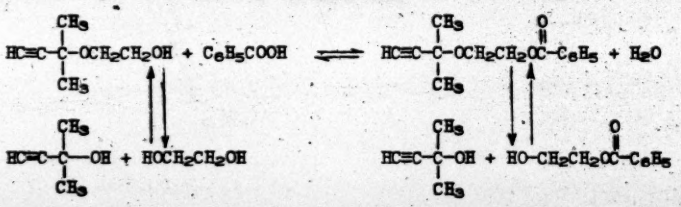
follows from the equation for its formation. Its analysis data and its conversion into esters likewise are evidence of the structure (I). The presence of a triple bond is borne out by the reaction of the β-hydroxy ethyl ether of dimethylacetenylcarbinol with a 2% aqueous solution of corrosive sublimate, yielding a curdy white precipitate. The β-hydroxy ethyl ether of dimethylacetenylcarbinol decolorizes a chloroform solution of bromine and an aqueous solution of potassium permanganate instantaneously.

In condensing ethylene oxide with dimethylacetenylcarbinol, we secured – in addition to the β-hydroxy ethyl ether of dimethylacetenylcarbinol – small quantities of the latter's further condensation with ethylene oxide, of which we isolated and analyzed the 88-93° fraction at 3.5 mm (d_{20}^{20} 1.038; n_D^{20} 1.4627; % OH 9.8), which proved to be a diglycol ether of dimethylacetenylcarbinol, together with traces of conversion products of the ethylene oxide itself.

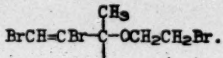
Of the derivatives of the β-hydroxy ethyl ether of dimethylacetenylcarbinol, we synthesized the acetate, butyrate, benzoate, the adipate, and products of bromination of the β-hydroxy ethyl ether of dimethylacetenylcarbinol and of the latter's acetate (see the subjoined table). The esters were prepared by reacting the β-hydroxy ethyl ether of dimethylacetenylcarbinol with acids or anhydrides.

Benzoic and adipic acids were recovered from their esters, the yields being low (40%). The low yields of the benzoate and adipate of the β-hydroxy ethyl ether of dimethylacetenylcarbinol is evidently due to the fact that the slow esterification is accompanied by a hydrolysis of the initial β-hydroxy ethyl ester of dimethylacetenylcarbinol and of the resultant esters, unwanted products being formed. A similar phenomenon was studied in detail by Nazarov and Romanov in the acyl esters of the β-hydroxy ethyl ether of dimethylvinylethynylcarbinol [1].

In the light of Nazarov's and Romanov's observation, it may be assumed that similar processes occur in the conditions we have employed for the synthesis of the specified esters, the reactions involved being as follows:

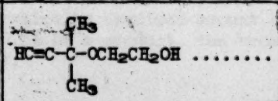
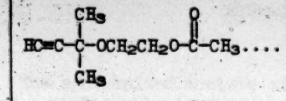
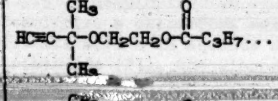
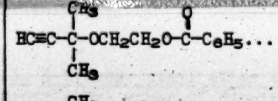
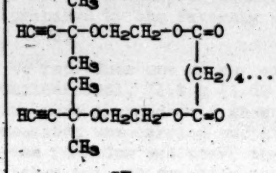
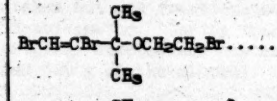
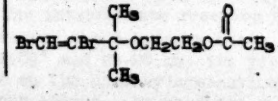


As we have already stated, the β-hydroxy ethyl ether of dimethylacetenylcarbinol does not give the well-known qualitative reaction for acetylenic hydrogen – precipitation with ammoniacal silver nitrate. To prove the existence of the triple bond directly, we undertook an attempt to brominate the β-hydroxy ethyl ether of dimethylacetenylcarbinol, hoping to secure its tetrabromide. The bromide was prepared by reacting bromine with a solution of the β-hydroxy ethyl ether of dimethylacetenylcarbinol in chloroform at -10 to -15°, without any chilling toward the close of the reaction. Instead of the expected tetrabromide, we found that the bromination products included a product whose bromine content was that of a tribromide: the β-bromoethyl ether of 3-methyl-1,2-dibromobuten-1-ol-3 (II):



(II)

List of Substances Synthesized from the β-Hydroxy Ethyl Ether of Dimethylacetenylcarbinol

No.	Formula	Boiling point	d_{20}^{20}	n_D^{20}	MR_D	
					Found	Computed
1		170.5-172° (760 mm)	0.9517	1.4500	36.10	35.70
2		91-93 (19-18.5 mm)	0.9808	1.4440	45.50	45.06
3		86-91 (6 mm)	0.9502	1.4370	54.60	54.29
4		132-133 (3-4 mm)	1.0576	1.5008	64.50	64.514
5		194-198 (3 mm)	1.0334	1.4670	98.20	97.15
6		125-135 (9-10 mm)	2.2560	1.6130	-	-
7		119-121 (3 mm)	1.7110	1.5370	60.30	60.39

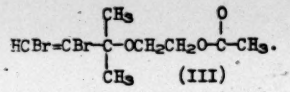
Analysis of this compound for a hydroxyl group yielded negative results.

When acetylene is brominated with liquid bromine or its solution, one usually gets a tetrabromide, in the main, the yield sometimes being as high as 90-95%. In our test, the process stopped when two atoms of bromine had been added and a double bond had been formed, preventing the further addition of bromine.

The absence of any reactivity of a double bond with regard to bromine has been observed in other instances as well [9-15].

The hindrance to the further addition of two more atoms of bromine to the β-hydroxy ethyl ether of dimethylacetenylcarbinol was apparently the fact that one of the carbon atoms attached to the triple bond had a fairly large radical attached to it. The substitution of bromine for the hydroxyl group was the

result of side reactions that took place during the reaction and during fractionation, and caused the evolution of hydrogen bromide, which reacted, in turn, with the dibromide's hydroxyl group to form the tribromide (II). To get rid of this side reaction we made another attempt to secure the dibromide by brominating the acetate of the β-hydroxy ethyl ether of dimethylacetenylcarbinol, using the theoretically required amount of bromine. In this experiment we secured a yield of 70.5% of a product, the bromine content of which was that of the dibromide (III):



(III)

The synthesized acetate of the β-hydroxy ethyl ether of 3-methyl-1,2-dibromobuten-1-ol-3 decolorized an aqueous solution of potassium permanganate; it did not decolorize a chloroform solution of bromine, however, nor did it yield a precipitate with a 2% aqueous solution of corrosive sublimate. In contrast to the tribromide (II), the dibromide (III) had a rather pleasant odor and displayed no irritant effect.

EXPERIMENTAL

1. β-Hydroxy ethyl ether of dimethylacetenylcarbinol. In synthesizing the β-hydroxy ethyl ether of dimethylacetenylcarbinol, we used dimethylacetenylcarbinol prepared by the Favorsky method [18], with a b.p. of 101-104°; d_{20}^{20} 0.8680; n_D^{20} 1.4200.

We reproduce one of our experiments. 406 g (4.83 moles) of dimethylethylacetenylcarbinol, 71.4 g (1.62 moles) of ethylene oxide, and 16 g of dimethylaniline were charged into an autoclave fitted with a stirrer and a thermocouple. The reaction was carried out at 145-150°, with constant stirring, for 8 hours. When the reaction was over, the autoclave was cooled, and the reaction products were taken out and fractionated from a flask fitted with a meter-high herringbone dephlegmator. During fractionation, the first thing to be distilled was the original dimethylacetenylcarbinol, up to 105° at standard pressure; this yielded 316 g of the alcohol. The fraction containing the β-hydroxy ethyl ether of dimethylacetenylcarbinol was collected at 82° (22-26 mm; 13 g).

The intermediate fraction distilled up to 82° (22-26 mm; 13 g). The fraction containing the β-hydroxy ethyl ether of dimethylacetenylcarbinol was collected at 82-84° and 25-26 mm; its yield totaled 101 g, or 74% of the theoretical, based on the dimethylacetenylcarbinol used. A small quantity of a dark-brown, viscous liquid – by-products – remained in the flask.

Externally, the β-hydroxy ethyl ether of dimethylacetenylcarbinol was a mobile, transparent, colorless liquid, which was soluble in benzene, acetone, chloroform, and ether, insoluble in water, and resisted the action of alkalies. It distilled at 170.5-172°, at standard pressure, without any signs of decomposition.

d_{20}^{20} 0.9517; n_D^{20} 1.4500; MR_D 36.10, computed 35.70. Found %: C 65.31; H 9.50; OH 13.18. $C_7H_{12}O_2$. Computed %: C 65.62; H 9.38; OH 13.28.

The number of hydroxyl groups was established by the phthalation method.

2. Acetate of the β-hydroxy ethyl ether of dimethylacetenylcarbinol. 64 g (0.5 mole) of the β-hydroxy ethyl ether of dimethylacetenylcarbinol and 153 g (1.5 mole) of acetic anhydride were placed in a flask fitted with a stirrer and a reflux condenser, and the mixture was carefully heated to the boiling point. Boiling was continued for 3 hours with constant stirring. Then 30 g of water was

added via the dropping funnel to decompose the excess anhydride, and heating was continued for another 40 minutes. The reaction mass was then cooled and processed with a saturated soda solution while chilled and constantly stirred, the soda solution being added from the dropping funnel until the mixture displayed a weakly alkaline reaction with phenolphthalein. Then the acetate was separated from the aqueous layer in a separatory funnel, its residue in the aqueous layer being extracted three times with ether, using 75 ml in each batch. The ether extracts were added to the acetate, which was twice washed with water until its reaction with bromocresolpurple was neutral and then desiccated with sodium sulfate. Then the sulfuric ether was driven out of the dehydrated product over a water bath, and the residue was fractionated in vacuum. The fraction representing the acetate of the β-hydroxy ethyl ether of dimethylacetenylcarbinol was collected at 91-93° and 19-18.5 mm). The yield of the acetate was 64 g (75.2% of the theoretical, based on the β-hydroxy ethyl ether of dimethylacetenylcarbinol). The acetate was a highly mobile, colorless, neutral liquid.

d_4^{20} 0.9908; n_D^{20} 1.4440; MR_D 45.40, computed 45.06. Found %: C 62.79; H 8.36; Saponification number 332. $C_9H_{14}O_3$. Computed %: C 63.50; H 8.23; Saponification number 329.

When the acetate of the β-hydroxy ethyl ether of dimethylacetenylcarbinol was reacted with a 2% aqueous solution of corrosive sublimate, it yielded a white precipitate; it also decolorized a chloroform solution of bromine.

3. Butyrate of the β-hydroxy ethyl ether of dimethylacetenylcarbinol. 64 g (0.5 mole) of the β-hydroxy ethyl ether of dimethylacetenylcarbinol, 55 g (0.62 mole) of butyric acid, 4 g of p-toluenesulfonic acid, and 100 ml of toluene were placed in a three-necked flask fitted with a stirrer, a reflux condenser, and a trap to catch the water formed during esterification. The reaction was carried out for 8 hours, with constant stirring, over a glycerol bath whose temperature was 150-160°. The water evolved during the reaction entered the trap together with the solvent vapors. The process was checked by the quantity of water recovered and by the acid number. By the end of the process 8.5 ml of water had been recovered, though 9 ml should have been evolved theoretically. The acid number was 5.6 mg of KOH by the end of the process. The processing and recovery of the ether were the same as before (Experiment 2). During fractionation the fraction representing the butyrate of the β-hydroxy ethyl ether of dimethylacetenylcarbinol distilled at 89-91° and 6 mm. The butyrate yield was 70 g (70.7% of the theoretical).

d_4^{20} 0.9502; n_D^{20} 1.4370; MR_D 54.60, computed 54.29; Found %: C 66.78; H 9.08; saponification number 277. $C_{11}H_{18}O_3$. Computed %: C 66.70; H 9.09; saponification number 283.

A yield of 79.5% of the theoretical of the ester was secured by esterifying the β-hydroxy ethyl ether of dimethylacetenylcarbinol with butyric anhydride.

The butyrate of the β-hydroxy ethyl ether of dimethylacetenylcarbinol decolorized a chloroform solution of bromine and formed a curdy white precipitate when reacted with a 2% aqueous solution of corrosive sublimate.

4. Benzoate of the β-hydroxy ethyl ether of dimethylacetenylcarbinol. The benzoate was prepared under the usual conditions (as in Expt. 3 above) by reacting 32 g (0.25 mole) of the β-hydroxy ethyl ether of dimethylacetenylcarbinol with 33.5 g (0.27 mole) of benzoic acid in the presence of 4 g of p-toluenesulfonic acid. During fractionation, the bulk of the ester distilled at 132-133° at 3-4 mm as a highly mobile, faintly colored liquid with an acid number of 1.28 mg of KOH. The yield was 22.5 g (40.80% of the theoretical).

d_4^{20} 1.0576; n_D^{20} 1.5008; MR_D 64.50, computed 64.51. Found %: C 72.39; H 6.82; saponification number 241. $C_{14}H_{16}O_3$. Computed %: C 72.40; H 6.90; saponification number 241.

The benzoate of the β-hydroxy ethyl ether of dimethylacetenylcarbinol reacted with a 2% aqueous solution of corrosive sublimate, yielding a slightly yellow, viscous precipitate, and decolorized a chloroform solution of bromine.

5. Adipate of the β-hydroxy ethyl ether of dimethylacetenylcarbinol. The adipate was synthesized under the conditions set forth above, by reacting 44.8 g (0.35 mole) of the β-hydroxy ethyl ether of dimethylacetenylcarbinol with 18.25 g (0.125 mole) of adipic acid in the presence of 2 g of p-toluenesulfonic acid. During fractionation, the bulk of the ester distilled at 194-198° and 3 mm as a brown oil with an acid number of 1.17 mg KOH. The yield was 18.3 g (40% of the theoretical).

d_{20}^{20} 1.0334; n_D^{20} 1.4670; MR_D 98.20; computed 97.15. Found %: C 67.40; H 8.24; saponification number 304.2. $C_{20}H_{30}O_8$. Computed %: C 65.60; H 8.22; saponification number 306.

The adipate of the β-hydroxy ethyl ether of dimethylacetenylcarbinol yielded a white precipitate with a 2% aqueous solution of corrosive sublimate and decolorized a chloroform solution of bromine.

6. β-Bromoethyl ether of 3-methyl-1,2-dibromobuten-1-ol-3. 32 g (0.25 mole) of the β-hydroxy ethyl ether of dimethylacetenylcarbinol and 200 ml of redistilled anhydrous chloroform were placed in a three-necked bottle fitted with a stirrer, a condenser with a calcium chloride tube, and a dropping funnel, and immersed in an ice-and-salt freezing mixture. Then 79.92 g (1 gram atom) of bromine was added from the dropping funnel while the mixture was constantly stirred and chilled (temperature of the freezing mixture: -10 to -15°). After the initial batches of bromine had been added, its color vanished immediately. Later the decolorization of the bromine slowed down, but it was observed until about half of the bromine had been added. After all the bromine had been added, the freezing mixture was removed, and the process continued for 3 hours at room temperature; but notwithstanding the rise in temperature the solution was not decolorized. Then the reaction mass was placed in a Claisen flask and distilled. Distillation was begun over a water bath, a water-jet pump being used and the chloroform and the unreacted bromine distilling over. The residue was fractionated with the use of an oil pump. Fractionation of the bromination product involved appreciable decomposition of the latter and the formation of gaseous substances that did not condense in the condenser. Fractionation yielded several fractions, one of which, a substance that distilled at 125-135° at 9-10 mm, was analyzed. It was a thick oil that darkened when exposed to light and was soluble in ether, acetone, and chloroform, slightly soluble in benzene, and insoluble in water. Its bromine content indicated that it was the β-bromoethyl ether of 3-methyl-1,2-dibromobuten-1-ol-3.

d_{20}^{20} 2.256; n_D^{20} 1.6130; Found %: Br 68.25. $C_7H_{11}OBr_3$. Computed %: Br 68.37.

Its bromine content was determined in accordance with [17]. The tribromide decolorized an aqueous solution of potassium permanganate; it did not decolorize a chloroform solution of bromine nor did it form a precipitate when reacted with a 2% aqueous solution of corrosive sublimate. When the tribromide was boiled with an alcoholic alkali for a long time, all three bromine atoms were nearly completely saponified.

Found: saponification number 446.1. $C_7H_{11}OBr_3$. Computed: saponification number 478.

We did not investigate the other fractions.

7. Acetate of the β-hydroxy ethyl ether of 3-methyl-1,2-dibromobuten-1-ol-3. 20 g (0.25 g atom) of bromine was added drop by drop, with constant stirring and

a freezing-mixture temperature of -10 to -15°, to 21.2 g (0.125 mole) of the acetate of the β-hydroxy ethyl ether of dimethylacetenylcarbinol and 100 ml of chloroform. Bromination was energetic at the start, but was much slower toward the close. After all the bromine had been added, the freezing mixture was removed, and the solution was allowed to stand overnight. When the process was over, the solution was yellow in color. The bromide was recovered as outlined above in Expt. 6. During fractionation, the acetate of the β-hydroxy ethyl ether of 3-methyl-1,2-dibromobuten-1-ol-3 distilled at 119-121° and 3 mm as a rather mobile, oily liquid that darkened when exposed to light, was insoluble in water, but freely soluble in organic solvents. The yield was 29 g (70.5% of the theoretical).

d_{20}^{20} 1.711; n_D^{20} 1.537; MR_D 60.30; computed 60.39. Found: M 314.60; % Br 49.30. $C_9H_{14}O_3Br_2$. Computed: M 329.84; % Br 48.50.

Its molecular weight was determined cryoscopically.

The presence of a double bond in the dibromide was confirmed by its decolorizing an aqueous solution of potassium permanganate.

SUMMARY

1. A method is outlined for the synthesis of the β-hydroxy ethyl ether of dimethylacetenylcarbinol, not previously described in the literature, by condensing dimethylacetenylcarbinol with ethylene oxide in the presence of a tertiary organic base.

2. The β-hydroxy ethyl ether of dimethylacetenylcarbinol has been employed to synthesize the acetoxy ethyl, butoxy ethyl, benzoxy ethyl, and adipoxy ethyl ethers of dimethylacetenylcarbinol.

3. A study has been made of the reaction of the β-hydroxy ethyl ether of dimethylacetenylcarbinol with bromine, it being found that only two atoms of bromine are added at the triple bond.

4. It has been found that two atoms of bromine are likewise added to the triple bond of the acetate of the β-hydroxy ethyl ether of dimethylacetenylcarbinol.

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RESEARCH ON THE KINETICS OF THE DEHYDRATION OF FORMIC ACID WITH SILICA GEL

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Sabatier distinguishes three different ways in which formic acid may be decomposed catalytically:

1) Dehydrogenation, catalyzed by metals: $HCOOH \rightarrow H_2 + CO_2$;

2) Dehydration: $HCOOH \rightarrow H_2O + CO$, accelerated by some metallic and metalloid oxides, salts, and acids.

3) Decomposition of formic acid, yielding formaldehyde: $2HCOOH \rightarrow HCHO + CO_2 + H_2O$, catalyzed by zinc and thorium oxides.*

Most metallic oxides are mixed catalysts, which promote the decomposition of formic acid as in (1) and (2) simultaneously.

Sabatier and Mailhe [1] have found that silica gel decomposes formic acid according to Equation (2), small amounts of formaldehyde also being formed. They likewise noted the catalytic action of the walls of the reaction tube, made of Jena glass, upon the decomposition of formic acid.

Hinshelwood, Hartley, and Topley [2] investigated the decomposition of formic acid in glass containers under static conditions at 240-300°. They found that both of the reactions (1) and (2) take place at the surface of the glass as monomolecular reactions, dehydration (Q_{CO} = 16,000 cal/mole and Q_{CO_2} = 28,000 cal/mole) predominating in one kind of glass, and dehydrogenation (Q_{CO} = 12,000 cal/mole and Q_{CO_2} = 24,500 cal/mole) predominating in another [3]. Diluting the acid with water (1:1) had no effect upon the velocity or course of the reaction.

Clark and Topley [4] made a study of the decomposition of formic acid by the static method at lower temperatures. The catalysts used were quartz, Pyrex, and sodium glass; the principal reaction products at 210° were carbon monoxide and water.

Nelson and Engelder [5] used the flow method in studying the part played by the walls of the reaction vessel in the decomposition of anhydrous formic acid. They secured gases, consisting chiefly of carbon dioxide and hydrogen, in quartz and in glass tubes. In a Pyrex tube decomposition set in at 250°, the reaction following Equation (1) at 350° (the percentage of carbon monoxide in the gas did not exceed 1.8%). The percentage of carbon monoxide in the gas at 600° was 18.1%. The gas evolved during the decomposition of formic acid in a quartz tube contained 1.6% of carbon monoxide at 350° and 3.6% at 550°.

Graber and Cryber [6] investigated the decomposition of 98% formic acid by the flow method. Of the catalysts tested (silica gel, ThO_2 + silica gel, TiO_2 + silica gel, P_2O_5 + silica gel, and Al_2O_3 and $AlPO_4$), they found the best to be

* In addition to formaldehyde, methanol may also be produced: $3HCOOH \rightarrow CH_3OH + 2CO_2 + H_2O$.

ThO_2 + silica gel. This catalyst was highly stable, the percentage decomposition of the formic acid being 94% at 280°, with 95% of the gas consisting of carbon monoxide.

The percentage of carbon monoxide in the gas when silica gel was used without any additive was a maximum at 240° and a rate of feed of formic acid equivalent to 1 ml of the acid vapor per ml of catalyst per minute. Under these conditions the percentage decomposition was only 32.3%. The highest percentage decomposition (93%) was attained at 300°, though the percentage of carbon monoxide dropped off as the temperature was raised still higher. In all our tests using silica gel catalysts neither formaldehyde nor methanol was found in the condensate; hence, reaction (3) did not take place.

This brief survey of the literature indicates that the walls of the glass vessel are not inert during the decomposition of formic acid. In Sabatier's and Nelson's researches the principal reaction occurring at the walls at 340-350° was dehydrogenation, whereas the principal reaction in Hinshelwood's experiments was dehydration. This may not represent any contradiction: each kind of glass accelerates the process dir[illegible] the experiments made by Clark at a comparatively low temperature (210°) and by Hinshelwood over a wide temperature range indicate that the predominant or sole reaction taking place in glass up to 300-350° is dehydration, dehydrogenation beginning to predominate as the temperature is raised. The temperature affected the course of the reaction pronouncedly in the experiments run by Adkins and Nissen [7] using glass wool, in which the CO/CO_2 ratio dropped fourfold when the temperature was raised from 320 to 360°.

In our research on the kinetics of the decomposition of formic acid with silica gel, we began with an investigation of the catalytic action of our reaction tube, finding that the tube walls did not affect the reaction perceptibly at temperatures below 300°. This enabled us to select the required temperature range.

In our investigation of the effect of glass wool, we found that it caused formic acid to decompose at an appreciable rate even at 280°, both reactions occurring simultaneously.

We used an 82% formic acid, inasmuch as Hinshelwood had found that a higher dilution of the acid with water (1:1) had no perceptible effect upon the process.

Lastly, in view of the findings of Graber and Cryber, we passed formic acid through the tube at a rather high volumetric rate of flow (6 ml of formic acid vapor per ml of catalyst per minute), thus ensuring the maximum selectivity and constancy of the decomposition reaction.

Under the experimental conditions set forth we secured a gas consisting almost entirely of pure carbon monoxide (98-99%). Thus, our findings served as a basis for determining the kinetics of the decomposition of formic acid by way of dehydration, uncomplicated by any side reactions. From these findings we computed the activation energy of the reaction and the coefficient of the exponential term. The activation energy of thermally deactivated Voskresensky silica gel ($Q = 15{,}400$ cal/mole) was found to be somewhat higher than that of the uncalcined catalyst ($Q = 14{,}500$ cal/mole), while the coefficient of the exponential term is considerably lower ($K_0 = 9.5 \cdot 10^7$ versus $K_0 = 7 \cdot 10^7$). The silica gel calcined at 1100-1200° was almost wholly inactive at temperatures below 300°, while above that temperature the reaction was predominantly one of dehydrogenation.

German silica gel likewise decomposed formic acid, yielding 98-99% carbon

monoxide. Its activity was nearly twice as great, its thermal stability lower, while its apparent activation energy before and after calcining differed but little from that of the first sample.

Adding lithium formate, sodium acetate, sodium hydroxide, or potash to the silica gel speeded up the dehydration of formic acid considerably. Potash displayed the greatest promoter action. The value of Q for the promoted silica gel was much lower than that of the unpromoted product.

The promoting action of potash is the same for active and deactivated silica gel, the acitivity increasing 3-4 times in each case. The compcsition of the gaseous reduction products secured with calcined silica gel (at 800°) and with the promoted silica gel did not differ from that secured with the initial sample. The inalterability of the course taken by the reaction when activated silica gel is replaced by thermally deactivated silica gel and the identical promoter action of traces of minerals on the active and calcined silica gels are evidence of the homogeneity of the active centers of the surface of the silica gel, which, as we had assumed previously, are located at its hydroxyl groups. It must therefore be assumed that the decrease in the activity of silica gel consequent upon calcining is due to a decrease in the number of active centers at the surface of the catalyst (a drop in the value of K_0) rather than to the destruction of the most active of these centers. On the other hand, if the active centers newly formed by promoter action consist of a mineral impurity and an active silica gel center at which the reaction occurs even when no promoter is present, these new centers may differ from the old ones qualitatively, while they may be fewer in number on the surface than the simple active centers on the surface of the unpromoted silica gel. We consider the fact that the activation energy and the K_0 of silica gel promoted with potassium carbonate are somewhat lower than those for a reaction using pure silica gel to be a confirmation of this hypothesis. When we compare the results attained in this research with those secured earlier, we find that mineral impurities activate silica gel for the reaction involving the dehydration of formic acid, whereas they poison the catalyst for the dehydration of alcohol or the vapor-phase hydrolysis of benzene halides [8].

Our experimental findings indicate that silica gel possesses much greater thermal stability in the dehydration of formic acid than in the dehydration of alcohol and vapor-phase hydrolysis. This may be due to the fact that the number of available active centers at the surface of the silica gel for the dehydration of formic acid is ten times as great as for the dehydration of alcohol and 1000 times as great as for the vapor-phase hydrolysis of benzene halides. As our findings show, the number of active centers on the surface of 1 g of silica gel, calculated from the optimum quantity of potash needed for promoting it in the dehydration of formic acid, is $1.7 \cdot 10^{20}$.

EXPERIMENTAL

Experimental and analytical procedures. The silica gel we used as a catalyst was first treated with concentrated nitric acid, washed with distilled water, and dried at 105-110°. The volume of the catalyst was 20 ml, its weight was 9-10 g, and the length of the catalyst bed within the tube was 6 cm. Calcining the catalyst at 800° caused practically no change in its specific gravity, whereas calcining it at 1200° caused its specific gravity to rise to 1.35.

We investigated the reaction kinetics, using catalysts of practically constant activity. When the activity of a given catalyst dropped 8 to 10%, it was discarded and replaced by a fresh one. It is a matter of course that the

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*Estimated from the comparative activity of silica gel and phosphate catalysts.

volumetric rate of flow must be kept unchanged during this operation. Inasmuch as the various catalyst batches consisted of grains of approximately the same size, while equal volumes of the catalyst had the same weight, these batches could be considered equivalent to one another. The activity of these equivalent batches, tested by the rate of decomposition of formic acid under identical experimental conditions, did not vary by more than 3-5%, as a rule.

The reaction tube had a partition P at its midpoint, formed by constricting the glass wall of the tube (Fig. 1), in order to keep the catalyst at a fixed point in the tube. The pocket for the thermocouple T, likewise made of Pyrex glass, was placed in the middle of the catalyst [illegible] by means of a glass stopper fitting over an outer ground-glass taper of the reaction tube. The pocket was tightly fitted to the glass stopper and was attached to it by means of the rubber tubing S. The receiver R was attached to the outer ground-glass tape of the other end of the reaction tube. The gas was fed into the reaction tube via the outlet O. In our apparatus, therefore, the formic acid and its vapor came in contact with nothing but glass, the catalyst being held in position at a fixed point of the tube without the use of any internal plugs of glass wool or asbestos.

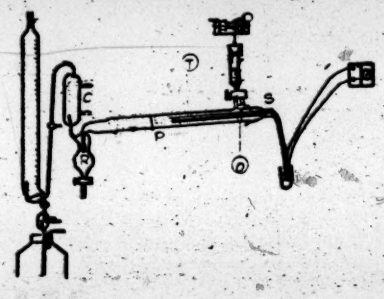

Fig. 1. Layout of apparatus for determining the kinetics of the dehydration of formic acid.

The vapor and gases passed through the catalyst and the receiver into the coil condenser C. From the condenser the gases passed through a three-way stopcock to an analysis apparatus or to a gas-measuring buret.

The formic acid was supplied at the constant rate of 0.22 ml/min by means of a specially designed piston device run by clockwork [3].

As our tests have shown, the reaction is extremely slow in the presence of silica gel below 170°, whereas above 300° the effect of the walls of the glass reaction tube become noticeable, catalyzing the reaction mainly along the lines of Equation (1). We therefore investigated the reaction kinetics in the 200-300° range, the gas consisting of 98-99% carbon monoxide in this range. The more active the catalyst, the higher the purity of the carbon monoxide.

We attributed the formation of carbon dioxide at temperatures in excess of 300° to the catalytic action of the (Pyrex) walls of the reaction tube, rather than to the action of another kind of active centers of the silica gel (dehydrogenation). This was borne out by the following experiment: In an experiment run at 333°, 1 ml of formic acid yielded 230 ml of gas, 9.4 ml of which was carbon dioxide. When we decomposed formic acid in the same tube with no catalyst present, but at a slightly higher temperature (350°), we secured 25 ml of gas, containing 10.5 ml of CO_2. Therefore, about as much carbon dioxide was formed in the empty tube as when the catalyst was present; i.e., the latter plays no part in the dehydrogenation reaction. On the other hand, the amount of carbon dioxide

formed at 418° with a silica gel calcined at high temperature (1100-1200°) was much higher than could be formed on the walls of the reaction tube at that temperature. This formation of carbon dioxide is due to a change in the structure of the catalyst, new active centers appearing on its surface.

Decomposition of formic acid by Pyrex and molybdenum glass, glass wool, and asbestos. As we see in Table 1, glass, asbestos, and glass wool accelerate each of the two reactions (1) and (2) involved in the decomposition of formic acid, as well as the overall process, differently.

TABLE 1

Decomposition of Formic Acid by Glass and by Asbestos

Nature of surface	Dimensions or weight	Temperature	Ml of gas evolved per ml of HCOOH	% composition of gaseous reaction products		
				CO_2	H_2	CO
Pyrex tube	480 cm^2	322°	6	43	42	15
Sheet asbestos...	8 g	322	70	17	19	61
Powdered molybdenum glass.....	10 g	322	60	38	39	23
Glass wool	1 g	322	66	36	34	30
Glass wool	1 g	280	18	14	14	71

In the empty (Pyrex) tube and with powdered molybdenum glass, Equation (1) predominates, whereas reaction (2) predominates when asbestos is used. When glass wool is used, dehydration predominates at 280°, whereas dehydrogenation predominates from 322° upward.

We see at a glance the high activity of glass wool, 1 gram of which (corresponding approximately to an internal plug) effects 12% decomposition of the formic acid at 322°.

Kinetics of the decomposition of formic acid with silica gel. As we see in Table 2, the percentage decomposition of anhydrous formic acid rises from 2% to 41% as the temperature is raised from 183° to 281°. The apparent activation energy of the reaction was 15,400 cal/mole, while the coefficient of the exponential term $K_0 = 2 \cdot 10^8$ (Fig. 2).

TABLE 2

Kinetics of the Dehydration of Anhydrous Formic Acid with Silica Gel

Temperature	Ml of gas evolved per ml of HCOOH *	Decomposition of HCOOH, %
183°	13.3	2.2
204	28.3	4.7
237	84.6	14.3
253	129.0	21.8
281	245.0	41.2

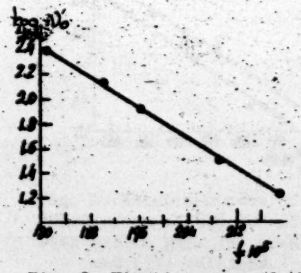

Fig. 2. Kinetic curve of the dehydration of anhydrous formic acid with silica gel.

Data on the kinetics of dehydration of 82% formic acid are given in Table 3 and Figs. 3 and 4. The kinetic constants of the reaction in the temperature range 242-292°: Q = 14,500 cal/mole and K_0 =

* The gas contained 98-99% CO.

$= 9.5 \cdot 10^7$, are somewhat different from the values found for the anhydrous acid.

The activity of the silica gel was diminished by at least 50% after calcining for 5 hours at 800°. Five hours of calcining at 1100-1200° effected a nearly complete deactivation of the silica gel, together with a marked change in its volume. In order to maintain a constant volumetric rate of flow of the formic acid, we used 20 ml of the catalyst, prepared by calcining 55 ml of the cold sample, in the tests run with the calcined silica gel.

TABLE 3

Kinetics of the Dehydration of 82% Formic Acid With Silica Gel

Catalyst	Temperature	Ml of gas evolved per ml of HCOOH	Decomposition of HCOOH, in %	Per cent CO in the gas
Silica gel	242°	37.5	8.1	99
	250	47.8	10.3	—
	262	63.6	13.7	98
	273	83.3	18.0	—
	294	144.0	31.0	97
Silica gel, calcined 5 hrs. at 800°	228	17.0	3.7	98
	240	23.0	5.0	98
	259	44.5	9.6	97
	283	84.0	18.1	95
Silica gel, calcined 5 hrs. at 1100-1200°	290	7.0	1.5	—
	351	33.5	7.2	—
	393	74.5	16.1	—
	418	120.0	26.0	—
	454	200.0	43.2	—

The gaseous reaction products secured with the silica gel calcined at 800° contained 1-2% less carbon monoxide than in the experiments with the uncalcined gel. This was not due to a change in the properties of the silica gel, but rather to the fact that the lowered activity of the thermally deactivated silica gel gave more scope for the reaction occurring at the walls of the reaction tube.

The kinetic constants of the reaction using silica gel calcined at 800° were: Q = 15,400 cal/mole and $K_0 = 7 \cdot 10^7$.

Thus, calcining the silica gel causes little change in the activation energy, but an appreciable decrease in the value of K_0.

The activity of the silica gel decreased so much after it had been calcined at 1100-1200° that the formic acid decomposed at a barely perceptible rate when it was used at 290°.

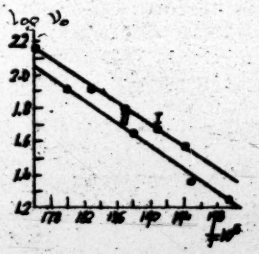

Fig. 3. Kinetic curves of the dehydration of 82% formic acid with silica gel: (I) uncalcined and (II) calcined.

Kinetics of the decomposition of formic acid with promoted silica gel. The data on the rate of decomposition of formic acid with silica gel impregnated with various admixtures are given in Table 4 and Figs. 4 and 5. As might have been expected, ammonia and ammonium chloride do not remain on the surface of the silica gel, and hence have no effect upon the latter's activity.

Sodium acetate, lithium formate, sodium hydroxide, and especially potash increase the activity of silica gel several hundred per cent.

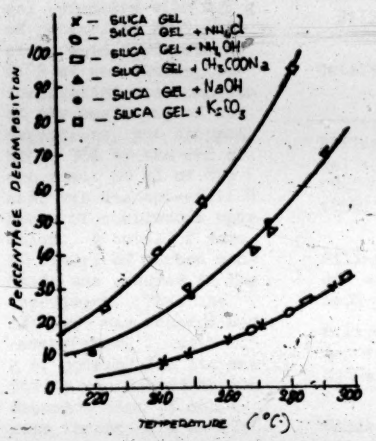

Fig. 4. Percentage decomposition of formic acid as a function of the temperature of the promoted silica gel.

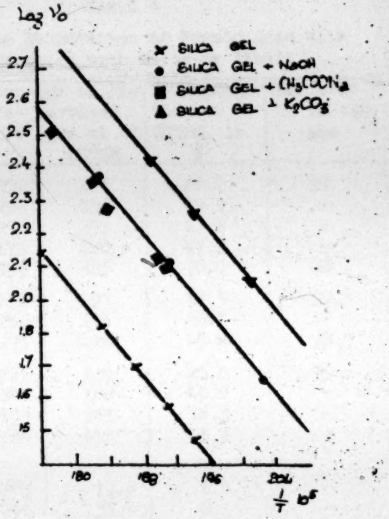

Fig. 5. Kinetic curves for the dehydration of formic acid with promoted silica gels.

Thus, in contrast to the reaction involved in vapor-phase hydrolysis, mineral admixtures do not poison the silica gel in the decomposition of formic acid, but rather promote it.

We see in Fig. 4 that the promoting action of sodium acetate and sodium hydroxide is almost identical, while the addition of potash increases the activity of the catalyst nearly 300%, though no change takes place in the gaseous products of the reaction.

The question naturally comes to mind: is the increase in the activity of the catalyst when it is promoted due to the formation of new active centers, in which the silica gel and the mineral admixture both participate, or is the increase in the catalyst's activity attributable to the mineral admixture alone, deposited on the silica gel? To answer this question we calcined 20 ml of silica gel at 1100-1200°, saturated it with a solution of 0.1 g of the lithium salt, and then tested the activity of this catalyst.

Tables 3 and 4 indicate that its activity increased. Even in the promoted form, however, this calcined silica gel displayed very little activity. Hence, a mineral admixture, deposited on a calcined, catalytically inactive silica gel, is by itself inactive. It must be assumed that the mineral admixture is adsorbed at the active centers of the silica gel, thus constituting new centers that possess increased activity. This is also borne out by the fact that an excess of the salt (such as more than 4% in the case of potash) has no effect upon the activity of silica gel (Table 6). We see in Table 4 that the value of K_0 and the activation energy drop somewhat when silica gel is promoted with a minera- admixture.

During a long test, run with 40 ml of silica gel promoted with 0.5 g of potash, at 295° and at an acid feed rate of 0.22 ml per minute, decomposition was complete at the beginning of the experiment, but dropped off to 76% by the end of the run. 50 ml of 82% acid was decomposed in 4 hours of continuous operation. A total of some 30 liters of carbon monoxide was secured in the experiment. Then the catalyst was removed and resaturated with 0.5 g of potash, and its activity was tested in the decomposition of anhydrous formic acid at 275°. It was found that the percentage decomposition of the anhydrous formic acid was likewise 100%.

TABLE 4

Kinetics of the Dehydration of Formic Acid With Silica Gel Promoted with Salts or Alkali

Catalyst	Temperature	Ml of gas evolved per ml of HCOOH	Decomposition of HCOOH, in %	Per cent CO in the gas
Silica gel + CH_3COONa (25%)*	250°	133	28.7	99
	252	136	29.3	–
	270	193	41.6	–
	275	220	47.5	–
	293	323	70.0	98
Silica gel + NaOH (1%)**	220	57	12.3	99.5
	250	133	28.7	–
	275	228	49.2	98.5
Silica gel + K_2CO_3 (1%)***	225	116	25.0	99.5
	241	188	40.6	–
	255	261	56.3	–
	284	433	93.5	–
Silica gel calcined at 1100-1200° for 5 hrs, + HCOOLi (1%)	265	11.0	2.4	–
	291	37.4	8.1	–
	325	74.4	16.1	–
	360	133.5	28.8	–

*Q - 13,000 cal/mol, $K_0 = 2.9 \cdot 10^7$
**Q - 14,000 cal/mol, $K_0 = 2.7 \cdot 10^7$.
***Q - 12,300 cal/mol, $K_0 = 3.6 \cdot 10^7$.

Kinetics of the decomposition of formic acid with a sample of German silica gel. This sample of silica gel had previously exhibited high activity in the vapor phase hydrolysis of chlorobenzene [8], though it did not possess high thermal stability. As we see by comparing the figures in Tables 3 and 5, this silica gel is nearly twice as active as the first sample in the dehydration of formic acid (Fig. 6). Figure 7 shows the kinetics of the reaction for the German silica gel: uncalcined (I) and calcined (II).

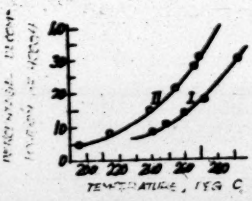

Fig. 6. Comparative activity of two samples of silica gel: I – Voskresensky; II – German.

Fig. 7. Kinetic curves for the dehydration of formic acid with German silica gel: I – uncalcined; II – calcined.

TABLE 5

Kinetics of the Dehydration of Formic Acid with a German Silica Gel

Catalyst	Temperature	Ml of gas evolved per ml of HCOOH	Decomposition of HCOOH, %	Per cent CO in the gas
Silica gel*	196°	19	4.1	99
	216	35	7.5	–
	240	64	13.8	–
	255	103	22.2	–
	267	129	27.8	–
	271	144	31.0	98
Silica gel, calcined at 800° for 24 hours**	259	27.2	5.8	96
	294	65.3	14.1	–
	311	93.7	20.2	82

*Q - 14,000 cal/mol, $K_0 = 5 \cdot 10^7$.
**Q - 14,600 cal/mol, $K_0 = 2 \cdot 10^7$.

The values of Q and K_0 for the reactions in which the German silica gel was used are not far from those found in the reactions with the Voskresensky silica gel.

Determination of the number of active centers on the surface of the (Voskresensky) silica gel. The data on the effect of the potash concentration upon the catalyst activity are given in Table 6. We found that increasing the potash concentration from 0.5% to 4% by weight of the silica gel increased the activity of the catalyst, whereas any further additions caused no further increase in activity.

TABLE 6

Effect of Potash Upon the Activity of Silica Gel in the Dehydration of Formic Acid
Wt. of silica gel 10 g; volume 22 ml; temperature 183°)

Added potash, grams	Gas evolved per minute, ml
0.0	2.0
0.05	5.3
0.10	7.0
0.20	13.0
0.30	15.0
0.40	18.0
0.60	18.0
1.00	18.0

TABLE 7

Effect of Potash Upon the Activity of Silica Gel in the Dehydration of 96% Ethyl Alcohol
(Wt. of silica gel 10 g; volume 22 ml; temperature 385°)

Added potash, grams	Gas evolved per minute, ml
0.0	11.0
0.001	10.5
0.006	3.0
0.010	2.2
0.020	0.7
0.030	0.4
0.050	0.2
0.100	0.2

On the assumption that one molecule of potash promotes one active center, we can calculate the number of active centers on the surface of 1 g of silica gel as follows:

$$A = \frac{0.4 \cdot 6.06 \cdot 10^{23}}{138 \cdot 10} = 1.7 \cdot 10^{20},$$

where 0.4 g is the optimum quantity of potash required to promote the given weight of silica gel; 138 is the molecular weight of potash; and 10 is the weight

of the silica gel to be promoted.

Table 7 gives the data on the effect of potash on the activity of silica gel in the dehydration of ethyl alcohol (volumetric rate of flow: 20 ml per minute).

Increasing the amount of potash added from 0.1% to 0.4% by weight of the silica gel practically deactivates the catalyst. Hence, the number of active centers on the surface of 1 g of silica gel in the dehydration of ethyl alcohol is: $A = 1.7 \cdot 10^{19}$.

SUMMARY

1. A study has been made of the kinetics of the dehydration of formic acid with two active samples of silica gel and with silica gel that had been thermally deactivated and promoted with mineral additives.

2. It has been found that the only reaction occurring in the temperature range of 200-300° when silica gel is present is the dehydration of the formic acid. The resultant gas is nearly pure carbon monoxide (98-99%).

3. It has been found that the apparent activation energy of the dehydration of formic acid is higher for thermally deactivated silica gels than for uncalcined silica gel, and somewhat lower for promoted silica gel. The value of K_0 decreases for the calcined and for the promoted silica gel. The composition of the gaseous reaction products (up to 300°) is the same with calcined, uncalcined, or promoted silica gel.

4. On the basis of the findings, the hypothesis is advanced that the active centers on the surface of silica gel are all alike and attached to its OH groups.

5. It has been shown that mineral admixtures, which deactivate silica gel nearly 100% in the vapor-phase hydrolysis of benzene halides and in the dehydration of alcohol, promote it in the dehydration of formic acid.

6. The number of active centers on the surface of 1 gram of silica gel has been calculated from the minimum quantity of salt required for the optimum promoting of silica gel in the dehydration of formic acid and for its poisoning in the dehydration of alcohol. It indicates that the ultraporosity of silica gel makes 10 times as many of its active centers accessible to the molecules of formic acid as to the molecules of ethyl alcohol.

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THE OXIDATION OF ALLYL AND CINNAMIC ALCOHOLS WITH A CHROMIC ACID MIXTURE

M. D. Bon

Allyl and cinnamic alcohols may be oxidized both at the double bond and at the alcohol group. Oxidizing allyl alcohol in neutral aqueous solution with potassium permanganate, E.E.Vagner [1] secured a yield of 80% of glycerol. N. Prilezhaev [2] also oxidized allyl alcohol at the double bond, using benzoyl peroxide dissolved in ether. Prilezhaev notes that practically the sole oxidation product under these conditions is glycidol. Volkov and Volosovich [3] found that when cinnamic alcohol is oxidized under the conditions laid down by E.E. Vagner, the corresponding glycerol is formed.

In view of the fact that various oxidizing agents display individually characteristic properties in some instances, we decided to oxidize allyl and cinnamic alcohols with a chromic acid mixture. Our experiments on the oxidation of allyl and cinnamic alcohols with a chromic acid mixture have shown that the action of a chromic acid mixture on unsaturated primary alcohols results in the formation of unsaturated aldehydes, which are further oxidized to unsaturated acids. The reaction of unsaturated primary alcohols with a chromic acid mixture is represented by simple equations that need not be set down.

EXPERIMENTAL

1. Oxidation of allyl alcohol by chromic acid mixture. 5 g of allyl alcohol, with a b.p. of 96-97.5°, d_4^{20} 0.8557, n_D^{20} 1.4134, was dissolved in 100 ml of water. Then the calculated quantity of chromic acid mixture was prepared (consisting of 15 g of potassium dichromate, 20 g of sulfuric acid, and 150 g of water). The mixture was added a drop at a time to the aqueous solution of the alcohol, the reaction mixture being carefully stirred. Thirty minutes after all the chromic acid mixture had been added the solution was distilled, the neutral and acid products being driven off with steam. The distillate had the sharp odor of acrolein. The distillate was neutralized with soda, and the neutral product was distilled from it.

The distillate, containing volatile neutral products, exhibited bright violet-red fluorescence with fuchsin sulfurous acid, formed a mirror with ammoniacal silver nitrate, and had the acrid odor of acrolein. Moist silver oxide was added to the distillate, and it was set aside to stand at room temperature. Upon standing, a mirror was formed, and a considerable amount of metallic silver was thrown down as a black powder. After the odor had grown much less pungent, the excess oxide and the metallic silver were filtered out, and the filtrate was evaporated and placed in a desiccator above sulfuric acid. The prismatic crystals of the silver salt crystallized out after some time had elapsed.

0.1575 g substance: 0.0952 g Ag. 0.1643 g substance: 0.0993 g Ag. Found %: Ag 60.42, 60.40. $C_3H_3O_2Ag$. Computed %: Ag 60.29.

Hence, the neutral products contained acrolein, which was converted by the moist silver oxide into acrylic acid.

The whole distillate residue left after the acrolein had been driven off was used in investigating the acids. The salt solution was evaporated to dryness over a water bath, and the dry residue was treated with absolute alcohol to leach out the sodium salts of organic acids. The extracted salts of organic acids were dissolved in water, and their aqueous solution was acidulated with sulfuric acid until its reaction was acid to litmus paper, after which it was distilled. The distillate, which had an acid reaction, was neutralized by boiling with lead carbonate, the excess lead carbonate was filtered out, and the filtrate was evaporated over a water bath. After the solution had cooled, the lead acrylate settled out. No non-volatile acids were detected.

0.0526 g substance: 0.0443 g $PbSO_4$. 0.1573 g substance: 0.1327 g $PbSO_4$. Found %: Pb 57.40, 58.42. $C_3H_3O_2Pb$. Computed %: Pb 57.86.

2. Oxidation of cinnamic alcohol with chromic acid mixture. 10 g of cinnamic alcohol, with a b.p. of 258° and a m.p. of 33°, was dissolved in 250 ml of water. Then a calculated quantity of chromic acid mixture was prepared, consisting of 30 g of potassium dichromate, 40 g of sulfuric acid, and 300 ml of water, and the mixture was added a drop at a time from a dropping funnel to the aqueous solution of the alcohol while the mixture was throughly stirred. Forty minutes after all the chromic acid mixture had been added, the neutral and acid products were distilled with steam. The distillate was neutralized with soda, and the neutral product was distilled from it.

The distillate, which contained volatile neutral products, displayed a reaction for a carbonyl group, yielded a characteristic color with fuchsin sulfurous acid, and formed a precipitate with a m.p. of 168-169° (from alcohol) when treated with phenylhydrazine.

0.1381 g substance: 14.8 ml N_2 (21°, 771 mm). Found %: N 12.48. $C_{15}H_{14}N_2$. Computed %: N 12.62.

All the distillate residue left after the cinnamic aldehyde had been driven off was used in investigating the acids. No volatile acids were found. The resultant salts were acidulated with sulfuric acid and then extracted with ether; the ether was driven off, leaving a colorless, thick oil which crystallized when left in a vacuum desiccator overnight. The substance was recrystallized from alcohol, yielding colorless crystals with a m.p. of 133-134°.

0.1822 g substance: 0.4912 g CO_2; 0.1005 g H_2O. Found %: C 72.84; H 5.12. $C_9H_8O_2$. Computed %: C 72.97; H 5.41.

These findings suffice to prove that the oxidation of cinnamic alcohol by a chromic acid mixture yields cinnamic aldehyde and cinnamic acid.

SUMMARY

1. Allyl and cinnamic alcohols have been oxidized with chromic acid mixture.

2. It has been shown that the oxidation of primary unsaturated alcohols with chromic acid mixture yields unsaturated aldehydes, which are then oxidized to unsaturated acids.

3. It has been found that when primary unsaturated alcohols are oxidized with a chromic acid mixture, the latter oxidizes the alcohol group, rather than the double bond.

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RESEARCHES ON THE CHEMISTRY AND TECHNOLOGY OF SYNTHETIC HIGH-MOLECULAR COMPOUNDS

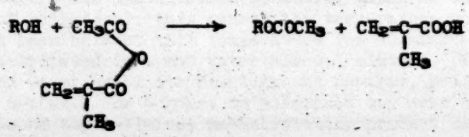
II, THE PREPARATION AND POLYMERIZATION OF ACETOMETHACRYLIC ESTERS OF CELLULOSE

A. A. Berlin and T. A. Makarova

There is very little information to be found in the literature (and what there is is incomplete) on the synthesis and the properties of cellulose esters and unsaturated esters. Aside from brief statements in the patent literature, and some data on the synthesis of cellulose crotonates [1], no papers have been published along these lines. Still, the introduction of double bonds into the chain of the macromolecule of the natural high-polymer opens up the prospect of the synthesis of three-dimensional copolymers of cellulose esters with various synthetic unsaturated compounds.

The present paper reports the initial results of our synthesis and polymerization of mixed acetomethacrylic esters of cellulose. Purified, previously activated cotton cellulose was used in esterification. At first we attempted to synthesize cellulose acetomethacrylate by reacting the cellulose with a mixture of methacrylic acid and acetic anhydride, by analogy with the synthesis of mixed esters of cellulose and saturated acids [2].

Our efforts along these lines met with failure, however, since we always obtained fully substituted esters of acetic acid instead of the mixed acetomethacrylic esters of cellulose. Evidently, in contrast to the mixed anhydrides of acetic and other low-molecular saturated acids, the acetomethacrylic anhydride formed by the reaction of acetic anhydride with methacrylic acid reacts with the hydroxyl groups of the cellulose as follows:



This compelled us to resort to the direct esterification of cellulose with methacrylic anhydride.

We synthesized the methacrylic anhydride from metacryl chloride and sodium methacrylate by heating their mixture over a boiling water bath, followed by processing the mixture at 35-40° in anhydrous ethyl ether. Various inhibitors were used in the synthesis to prevent polymerization. The maximum yield (68%) of the methacrylic anhydride was secured by boiling the reaction mixture for 3 hours over a boiling water bath with 0.5% of cuprous chloride and then treating the mixture for 3 hours with boiling sulfuric ether. Quinhydrone ensured a

yield of about 54%, while the yield of the anhydride was only 41% when this inhibitor was not used.

In contrast to acetic anhydride, methacrylic anhydride reacts with water extremely slowly, even when sulfuric acid is present. When equal volumes of acetic anhydride and a 10% solution of sulfuric acid were mixed together, for instance, hydrolysis was complete within 2-2.5 minutes, whereas methacrylic anhydride did not react with water even after 2-3 days when the same reagent proportions were employed. The comparatively lower activity of methacrylic anhydride excludes the possibility of using it as a dehydrating agent in the activation or esterification of cellulose.

In addition to methacrylic anhydride, we likewise tested methacryl chloride as a methacrylating agent, synthesizing it from methacrylic acid and phosphorus trichloride, using cuprous chloride or hydroquinone as polymerization inhibitor. We found that the yield of methacryl chloride depends upon the order in which the reagents are added and, to a much lesser extent, upon the nature of the polymerization inhibitor employed.

The best results (68% yield) were secured when the methacrylic acid was added to the phosphorus trichloride and when cuprous chloride (0.5% by weight of the methacrylic acid) was used as the polymerization inhibitor.

The following procedure was employed in acylating cellulose with methacrylic anhydride or with a mixture of methacrylic and acetic anhydrides.

The cotton cellulose was saturated with an equal weight of glacial acetic acid and kept for 12 to 20 hours in a hermetically sealed glass container. After it had "ripened", the cellulose was gradually added to the acylating mixture at 15-20°. An excess of 50% over the quantity of methacrylic anhydride theoretically necessary was used, while the quantity of acetic anhydride was enough for partial substitution of the OH groups and for the binding of the water contained in the acetic acid and in the cellulose. In some of the tests the acetic anhydride was added merely as a desiccating agent. The modulus of the reaction mixture varied from 1:8 to 1:14. 8-12% of sulfuric acid (sp.gr. 1.84) or 0.5% of perchloric acid was used as the esterizing catalyst per 100% of the mixture. Acylation was carried out at 30-35° (up to 45°), with 0.1-0.5% of hydroquinone added as a polymerization inhibitor.

The product dissolved completely only after tetrachloroethane or glacial acetic acid was added to a sample that had undergone 6-10 hours of acylation. The reaction mixture was desulfurized by adding water to the reaction mixture (0.5 ml per g of cellulose); this caused the temperature to rise to 40°. After the mixture had been held at this temperature for 40 minutes, the reaction product was precipitated in a hot water-alcohol mixture. The ester was washed with alcohol and water until its reaction was neutral, dried at 20°, and then extracted with methanol for 4 hours to eliminate any adsorbed methacrylic anhydride. The yield of the cellulose methacrylation product was 138-140% of the cellulose by weight.

We found that this product was soluble in glacial acetic acid at the boiling point and in tetrachloroethane in the cold. It did not dissolve in chloroform, acetone, or benzene, even at high temperatures. The number of combined methacrylic groups was determined by the Knorr bromine number method. In view of the fact that the products of the destruction of cellulose might throw the analysis results out of kilter, the double bonds were determined in the distillate after the saponification had been acidulated with phosphoric acid. The procedure we employed was as follows.

About 2 g of the ester was treated with 75% alcohol for an hour at 56-67°. Then a 0.5 N NaOH solution was added, and the mixture was kept at that temperature for another hour, after which the sample was kept at room temperature for 2 hours. The saponification number of the ester was determined by titrating it with a 0.5 N acid and phenolphthalein. Then the precipitate was filtered out and washed with water until its reaction for SO_4" and double bonds was negative. Cuprous chloride was added to the filtrate, which contained sodium sulfate, acetate, and methacrylate, alcohol, and cellulose destruction products, and the whole was evaporated to a volume of 50-60 ml over a water bath, after which the mixture was acidulated with orthophosphoric acid, and the acids formed as the result of saponification were driven off. The percentage of methacrylic acid was determined from the bromine number of the distillate. The percentage of acetic acid was determined by means of acidimetric titration, measuring the difference between the total acidity and the percentage of unsaturated acid. Though we carried out the reaction in acetic acid, even excluding acetic anhydride from the acylation mixture, we were unable to secure a product that contained more than one methacryl group per 30 glucose residues of the cellulose.

We have thus established that under the experimental conditions selected the reaction involves chiefly a substitution of the acetyl groups for the cellulose OH groups. In all these instances, apparently the methacrylic anhydride reacted with the acetic acid used to activate the cellulose, rather than with the cellulose itself. By and large, the resultant acetomethacrylic anhydride reacted with the cellulose as indicated above, only an insignificant proportion of the anhydride or that which did not react with the acetic acid replacing the cellulose OH groups by methacryl radicals.

When acetic acid was excluded from the reaction zone completely, and the cellulose (previously activated with methacrylic acid, in the presence of sulfuric acid totaling 4% of the cellulose by weight) was acylated in a mixture consisting of methacrylic anhydride, used in 100% excess over the quantity theoretically required, methacrylic acid, and 8-12% of sulfuric acid, the methacrylation process was extremely slow. The resultant product contained one methacryl group per 7 glucose residues and was wholly insoluble in various organic solvents.

To secure a mixed cellulose ester, the methacrylic cellulose derivative was then acetylated with a mixture consisting of acetic anhydride, acetic acid, and a catalyst — sulfuric acid. Enough acetic anhydride was added to replace the remaining free OH groups, plus a 50% excess. The quantity of sulfuric acid did not exceed 8% of the methacrylation product by weight. The acylation bath factor was 1:8.

Analysis of the product of this supplementary acetylation showed that the number of methacryl groups in the ester had dropped from 0.42 to 0.15, while the number of acetyl groups had increased. Hence, these experiments proved that the acetylation process involved acidolysis or re-esterification, resulting in a partial demethacrylation.

We were able to replace an even greater proportion of the cellulose OH groups by methacryl radicals by activating the cellulose for 24 hours with 87% formic acid, and then substituting methacrylic acid for the latter. When this was done, the very same methacrylating mixture enabled us to secure a product containing 1.06 methacryl groups per glucose residue after 20 hours of reaction at 40-45°. This product was also insoluble in organic solvents. Supplementary acetylation reduced the number of methacryl groups to 0.73 per glucose residue. This made the products of supplementary acetylation soluble in tetrachloroethane, chloroform, and glacial acetic acid.

Alongside this study of acylation with methacrylic anhydride, we [illegible]

tested the esterification of cellulose with methacryl chloride. For this reaction the cellulose was given a preliminary treatment with boiling dichloroethane for 2 hours, and then a little at a time was placed in a mixture of pyridine and dichloroethane. A solution of sulfur in carbon tetrachloride, totaling 0.5-1% of sulfur by weight of the methacryl chloride, was added to the acylating mixture to prevent polymerization during the esterification process. The amount of methacryl chloride used was calculated on the basis of replacing all the OH groups in the cellulose, plus a 50% excess above the theoretically required quantity. The acylating bath factor was 1:20. After the cellulose had been added, the temperature of the mixture was raised to 100°, and the reaction was continued for 10 hours. The esterification product was isolated as a fibrous mass by the use of methanol. Two successive methacrylations yielded a product that contained one methacryl group per 5 glucose residues.

The reaction of methacryl chloride with cellulose involved quite extensive destruction of the latter, so that the yield of the methacrylation product did not exceed 50-55%, dropping to 20-22% after two successive processings. The destruction was even greater when an alkali cellulose desiccated with absolute ethyl alcohol and processed with methacryl chloride.

These experiments proved that methacryl chloride is unsuitable for the esterification of cellulose, so that we did not use this reagent in our subsequent experiments.

The acetomethacrylic esters of cellulose prepared earlier, by two-stage esterification with methacrylic anhydride and acetic anhydride, can be partially hydrolyzed by one of the methods employed for producing an acetone-soluble cellulose acetate.

We also secured an acetomethacrylic ester of cellulose containing hydroxyl groups by methacrylating a secondary cellulose acetate (54.5% CH_3COOH) at 45° with methacrylic anhydride dissolved in acetone. The reaction was stopped when 0.2-0.25 of the hydroxyl groups had been replaced by methacryl radicals. The "secondary" cellulose acetomethacrylate thus produced was readily soluble in chloroform and in dichloroethane, besides being soluble in acetone and ethyl acetate.

We made a study of the acetomethacrylic esters of cellulose activated with formic acid and of the methacrylation products of the secondary cellulose acetate to determine the feasibility of polymerizing them and of copolymerizing them with some low-molecular monomers. We polymerized the cellulose acetomethacrylates in sealed ampoules at 65 ± 0.5° in 10% acetone solutions (for the "secondary" acetomethacrylate) or tetrachloroethane solutions (for the acetylation product of cellulose monomethacrylate).

Benzoyl peroxide (3-5% of the respective cellulose ester by weight) was added to the solution to initiate the polymerization process.

Our experiments indicated that a gel insoluble in organic solvents is formed even when the cellulose acetomethacrylate contained only one methacryl group per 15 glucose residues.

Increasing the percentage of methacryl groups increases the rate of gelation. For example, an insoluble jellylike product was formed after 4.5 hours of polymerization of the "secondary" cellulose acetomethacrylate in which 0.2 of the hydroxyl groups had been replaced by $CH_2=C(CH_3)-CO$, whereas only 1.5 hours was required for the complete conversion of an esterified product, in which 0.7 of the hydroxyl had been replaced by methacryl groups, into an insoluble gel under the same conditions. The viscosity did not increase during the polymerization of the cellulose acetomethacrylates, indicating that these

cellulose derivatives possess three-dimensional structures without passing through the stage of soluble polymers [3].

We copolymerized the cellulose acetomethacrylates with low-molecular monomers under the same conditions. In the first stage of our research we explored the feasibility of copolymerizing 1 to 10% with the methylacrylate and the dimethacrylate of diethylene glycol. Preliminary tests showed that adding these monomers results in the formation of infusible and insoluble copolymers. An attempt to effect the three-dimensional polymerization and colpolymerization of cellulose acetomethacrylates without a solvent, in a thin layer (a film) on a glass or metal surface met with failure. No insoluble or infusible polymer was found even after 72 hours of heating to 80° in a thermostat. Apparently it is extremely hard for the radicals to encounter the double bonds of the function groups under these conditions, to which there must be added the inhibitory action of atmospheric oxygen.

EXPERIMENTAL

Synthesis of methacryl chloride. One-third mole of phosphorus trichloride and 0.5% cuprous chloride by weight of the methacrylic acid were placed in a three-necked flask fitted with a thermometer, a reflux condenser, and a dropping funnel. One mole of methacrylic acid was gradually added to the flask from the dropping funnel at 60-70°. Then the contents of the flask were kept at 60-70° for another 15 minutes, and heating was stopped. Two hours later the upper layer, consisting of methacryl chloride, was decanted. The 95-97° fraction was collected during distillation, the yield being 65-68° of the theoretical. n_D^{20} 1.4440; MR_D 25.2; computed 25.40.

Synthesis of methacrylic anhydride. One mole of finely pulverized sodium methacrylate, dried at 110°, and 0.5% of cuprous chloride were placed in a three-necked flask fitted with a stirrer, a reflux condenser, and a dropping funnel. One mole of methacryl chloride was gradually added from the dropping funnel, while the stirrer was turning continuously.

After all the methacryl chloride had been added to the reaction mixture, the temperature of the bath was gradually raised to 100°, and the reaction mass was stirred for 3 hours at that temperature. Then the bath temperature was reduced to 30-40°, 60 ml of anhydrous sulfuric ether was added, and the whole was kept for another three hours at 30-40°. The reaction mixture was then transferred to a Claisen flask, and the methacrylic anhydride was distilled in vacuum. A fraction with a b.p. of 89° at 5 mm was collected. The yield was 66-68% of the theoretical. n_D^{20} 1.4540; MR_D 40.5; computed 39.88; the bromine number was 209 (207.8 theoretically).

Esterification of cellulose with methacrylic anhydride. Cleaned cotton cellulose was wetted with 87% formic acid, the proportions being 1:3, and kept at 20° for 24 hours. The cellulose thus processed was then washed 3-4 times with methacrylic acid and squeezed out until its weight was three times its original value.

The esterifying mixture was prepared, with a bath factor of 12, from methacrylic anhydride, allowing enough for the complete replacement of 3 OH groups plus 50-100% excess, methacrylic acid, and H_2SO_4 amounting to 8% of the cellulose by weight. The cellulose was added to the esterifying mixture at 10-15° with constant stirring, the process taking 1-1.5 hours. Then the temperature was gradually raised to 45° and kept there for 18-19 hours with continuous stirrer operation.

The reaction mass became homogeneous after 12-15 hours, though large quantities of fiber were observed under themicroscope, even when the reaction was

stopped (after 20 hours). The cellulose ester was thrown down in a heated 1:1 mixture of water and alcohol, and then it was washed with hot water and with alcohol. The product was extracted with ether for 4 hours to eliminate the methacrylic acid adsorbed by the ester.

Acetylation of the cellulose monomethacrylate. The cellulose monomethacrylate was added at 8-10°, with constant stirring, to an acetylating mixture consisting of enough acetic anhydride to replace the rest of the OH groups plus a 20-50% excess, acetic acid, and sulfuric acid (representing 8% of the monomethacrylate). After all the monomethacrylate had been added to the mixture, the temperature of the latter was gradually raised to 35-40°, and the reaction was carried out at that temperature for 5-6 hours. Then 5 ml of water was added (as a desulfurizer), and the reaction mass was precipitated in hot water one hour later. The resultant product was washed with water and dried at 20°.

Esterification of the secondary acetylcellulose with methacrylic anhydride. Calcined sodium carbonate and enough methacrylic anhydride to replace the hydroxyl groups in the acetylcellulose were added to a 15% acetone solution of "secondary" acetylcellulose, containing 2.2-2.3 acetyl groups per glucose residue. The mixture was heated to 45° and kept at that temperature until a thick gel was formed, after which the temperature was lowered to 25°, and the mixture was allowed to stand for 24 hours. Then a small quantity (5-7 ml) of water was added, the solution was diluted, and the insoluble salts were thrown down. The transparent water-acetone solution of cellulose acetomethacrylate was decanted, and the resulting product was precipitated with water, washed, and dried at 20°.

SUMMARY

1. The conditions required for the synthesis of the acid chloride and the anhydride of methacrylic acid have been defined, and these substances have been identified.

2. It has been found that using methacrylic acid mixed with acetic anhydride as the esterifying agent results in the formation of cellulose acetates.

3. It has been learned that esterifying cellulose with methacrylic anhydride, using acetic acid as the medium, likewise results in the formation of cellulose acetates.

4. Methacrylating cellulose with the acid chloride of methacrylic acid in pyridine and the reaction of the acid chloride with alkali cellulose are both accompanied by considerable destruction and do not make it possible to add more than one methacrylic group for every 8 glucose residues.

5. Cellulose that has been given a preliminary formic-acid treatment can be esterified with methacrylic anhydride when no acetic acid is present, yielding a monosubstituted cellulose methacrylate.

6. It has been found that further acetylation of the resultant cellulose methacrylates, with a view to the production of soluble acetomethacrylic derivatives, is accompanied by re-esterification, resulting in the partial substitution of acetyl groups for the methacryl ones.

7. It has been demonstrated that cellulose acetomethacrylates in solution, with benzoyl peroxide present, can be polymerized or copolymerized with esters of methacrylic acid, yielding infusible polymers and copolymers that are also insoluble in organic solvents.

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THE CONDENSATION OF ETHYLENE OXIDE WITH HOMOLOGS OF BENZENE

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The condensation of ethylene oxide with benzene or with its homologs takes place in the presence of aluminum chloride, boron fluoride, and other catalysts employed in the Friedel-Crafts reaction. The feasibility of synthesizing β-aryl derivatives of ethyl alcohol by this method is mentioned in several patents [1]. These patents, however, do not give examples of the condensation of ethylene oxide with disubstituted benzenes, to begin with, and second, no study appears to have been made of the condensation process or of the structure of the resultant alcohols, the latter being more or less evident only in the condensation of ethylene oxide with heterocylcic compounds [2].

Of these condensations, the only one that has gained acceptance is the condensation of ethylene oxide with benzene to produce β-phenylethyl alcohol, a rose oil that is a high-quality raw material for the perfumery industry. Condensation conditions have been worked out for the synthesis of oil of roses that give a yield of this alcohol as high as 65% of the theoretical.

At first a coordination compound of ethylene oxide and aluminum chloride is formed [3], which then reacts with the benzene to form β-phenylethyl alcohol and a certain amount of dibenzyl.

The yield of β-phenylethyl alcohol is a maximum when the process is carried out at a temperature no higher than 5-10°, and the ethylene oxide is added in a mixture with air or an inert gas. Air or nitrogen is bubbled through the reaction mass to remove the hydrochloric acid from the reaction zone, as otherwise it would combine with the ethylene chloride to form ethylene chlorohydrin, an unwanted by-product.

When homologs of benzene are condensed with ethylene oxide, the course of the reaction and the optimum conditions depend upon the nature and the quantity of the groups or atoms replacing the benzene hydrogen atoms.

Toluene is condensed fairly readily with ethylene oxide under conditions that resemble those used for the synthesis of β-phenylethyl alcohol. The yield of β-p-tolylethyl alcohol is 40-45% of the theoretical, based on the toluene consumed. Slight fluctuations of the reaction temperature, of the order of 5-15°, do not affect the alcohol yield.

The condensation of ethylene oxide with a mixture of isomeric xylenes is an incomparably more capricious reaction. The reaction temperature must not exceed 0-5°, and even under such mild conditions the yield of β-xylylethyl alcohols does not exceed 30% of the theoretical, and is always accompanied by

side reactions. Raising the reaction temperature to 20-30° makes the side reactions predominate, resulting in the formation of a mixture of high-boiling hydrocarbons, out of which a large quantity of diphenyl crystallizes after some time. The formation of the diphenyl proves that the xylene loses methyl groups, in addition to side processes that are unknown to us.

The yield of β-xylylethyl alcohols is barely 10% when the reaction temperature is raised to as little as 10-15°.

We were able to separate the β-xylylethyl alcohol we synthesized into two fraction by repeated fractionation in vacuum: Fraction 1 – b.p. 110-112° at 2 mm, and Fraction 2 – b.p. 115-117° at 2 mm.

To determine the position of the ethylol group after the condensation with the benzene homologs, we oxidized the synthesized alcohols with dilute nitric acid, securing the acids that corresponded to β-p-tolylethyl alcohol, β-o-xylylethyl alcohol, and β-m-xylylethyl alcohol. The melting points of the resultant acids agreed with the melting points given in the literature [4].

Ethylene oxide can be condensed with chlorobenzene only at 100° [2]. At lower reaction temperatures the yield of the alcohol is barely 1-2%.

We were unable to condense ethylene oxide with dichlorobenzene (a mixture of the ortho and para isomers), either by boiling or by working in a solution of nitrobenzene.

EXPERIMENTAL

β-p-Tolylethyl alcohol. 150 g of toluene and 50 g of $AlCl_3$ were charged into a four-necked flask, fitted with a stirrer, a reflux condenser, a tube for the supply of ethylene oxide mixed with air, and a thermostat. The free end of the reflux condenser was connected to a water-jet pump that served to draw off the hydrochloric acid formed during the reaction. The flask was immersed in a bath filled with snow and salt.

The ethylene oxide (75 g) was poured into a Würtz flask, the side tube of which was connected via a tee to an air line. At the start of the reaction the flask containing the ethylene oxide was not heated, the quantity of ethylene oxide reaching the reaction flask being governed by the force of the air stream drawing it in. After 2-3 hours had elapsed, when half the ethylene oxide had been drawn off, the flask was placed in hot water, the reaction being stopped as soon as all the ethylene oxide had been drawn off (a total of 4-5 hours). The temperature in the reaction flask must not exceed 5-10° throughout the reaction. Then the reaction mixture was poured over ice, hydrochloric acid was added, and the upper layer was decanted, washed with water and with soda until its reaction was neutral, and desiccated with calcined potash; then the toluene was driven off, and the alcohol was distilled in vacuum.

β-p-tolylethyl alcohol is an oily liquid with a rather fragrant aromatic odor. B.p. 103° at 4 mm; d^{19} 0.997; n_D^{21} 1.5275; MR_D found 41.964; computed 41.686.

β-Xylylethyl alcohols. A xylene mixture with a b.p. of 137-145° was poured into the reaction flask described above, the proportions being the same as before. The reaction was similar to the preceding one, but the chilling of the flask had to be more efficient: the temperature within the flask could not exceed 5°.

The β-xylylethyl alcohol was divided into two fractions after repeated fractionation in vacuum: Fraction 1 with a b.p. of 110-112° (2 mm), and Fraction 2 with a b.p. of 115-117° (2 mm).

A high-boiling fraction, b.p. 165-167°, that contained no ethylol groups was also recovered; it was a mixture of hydrocarbons that we did not investigate any further. Diphenyl, with a m.p. of 70°, crystallized out of this fraction after some time had elapsed.

β-Xylylethyl alcohols are oily liquids with a rather fragrant flowery odor.

o-Xylylethyl alcohol: b.p. 110-112° (2 mm); d^{18} 0.9915; n_D^{21} 1.5310; MR_D computed 46.304; found 46.747.

m-Xylylethyl alcohol: b.p. 115-117° (2 mm); d^{18} 0.993; n_D^{21} 1.5290; MR_D computed 46.304; found 46.598.

When we determined the percentage of alcohol in the synthesized alcohols by the acetylation method, we found that β-p-tolylethyl alcohol contained 102% alcohol, while β-o-xylylethyl alcohol (Fraction 1) contained 103%, and β-m-xylylethyl alcohol (Fraction 2) contained 101%.

We used the method of oxidation with dilute nitric acid (2 parts of acid, sp.gr. 1.5 + 3 parts of water) to determine the structure of the synthesized β-arylethyl alcohols. We believed that it was the ethyl group containing an oxygen atom, rather than the methyl groups, that underwent oxidation first. We succeeded, in fact, in securing the acids that corresponded to our alcohols; viz.: oxidation of β-tolylethyl alcohol yielded p-toluic acid with a m.p. of 181° (181° in the literature); while oxidation of Fraction 1 of the β-xylylethyl alcohol yielded a mixture of o-xylic acid with a m.p. of 144° (143° in the literature) and hemimellitic acid with a m.p. of 197° (197° in the literature).

Oxidation of Fraction 2 of the xylylethyl alcohol yielded symmetrical m-xylic acid with a m.p. of 166° (167° in the literature).

The synthesis of these acids was confirmed by titration, in addition to the melting points given above.

SUMMARY

1. The following alcohols have been synthesized by condensing toluene and xylene (a mixture of isomers) with ethylene oxide: β-p-tolylethyl alcohol, β-o-xylylethyl alcohol, and symmetrical β-m-sylylethyl alcohol.

2. Oxidation of the alcohols with dilute nitric acid yielded: p-toluic acid, o-xylic acid, hemimellitic acid, and sym-m-xylic acid, which enabled us to evaluate the structure of the synthesized β-aryl-substituted ethyl alcohols.

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THE ORGANOLITHIUM COMPOUNDS OF 1,2-BENZANTHRACENE AND THEIR TRANSFORMATIONS

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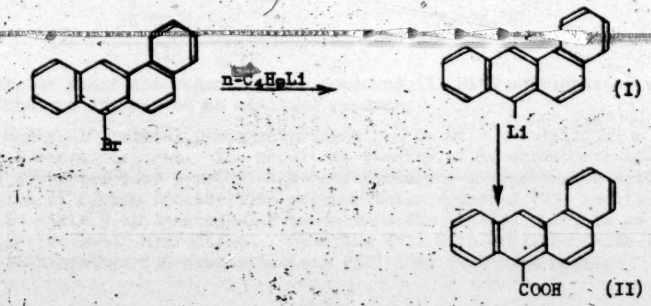
The organic compounds of lithium are now as accessible as the Grignard reagents. Organolithium compounds are secured even more readily than organomagnesium compounds for the anthracenes [1] and the 1,2-benzanthracene derivatives, while their high reactivity makes them highly valuable in syntheses.

The simplest method of preparing organolithium compounds, consisting of reacting lithium with halogen derivatives of hydrocarbons, fails to produce lithium derivatives of 1,2-benzanthracene, as was found to be the case with the anthracenes [1]. When we react 10-bromo-1,2-benzanthracene with lithium in ether, we get only traces of the organolithium compound, the main reaction product being 1,2-benzanthracene. Much more 1,2-benzanthryl-10-lithium is produced in an ether-benzene medium, but even under these conditions the amount of hydrocarbon produced is extremely high. We have succeeded in securing high yields of organolithium compounds of the 1,2-benzanthracene series by reacting n-butyllithium or phenyllithium with the corresponding halogen derivatives.

The reaction between 10-bromo-1,2-benzanthracene and n-butyllithium takes place in a few minutes; the resultant 1,2-benzanthryl-10-lithium (I) is smoothly converted into the carboxylic acid (II) by carbonic acid. The organolithium compound (I), which is stable in diethyl ether, can react with n-butyl bromide, prepared in a double decomposition reaction, to yield 10-n-butyl-1,2-benzanthracene, so that prolonging experiments on the synthesis of the organometallic



compound results in a decrease in the latter's yield. The secondary reaction involving the formation of 10-n-butyl-1,2-benzanthracene may be speeded up by adding n-butyl bromide to the reaction mixture, thus raising the yield of the butyl derivative to 35%. Phenyllithium reacts much more slowly with

10-bromo-1,2-benzanthracene than does n-butyllithium: the maximum yield of the organolithium compound is secured by heating the reagents to 40° for 45 minutes.

1,2-Benzanthryl-10-lithium (I) reacts readily with alkyl iodides. Compound (I) reacts with methyl iodide to yield 80% of 10-methyl-1,2-benzanthracene (III, R = CH_3), no matter whether n-butyllithium or phenyllithium is used to synthesize the organometallic compound. In synthesizing other homologs of 1,2-benzanthracene, the compound (I) should be prepared with phenyllithium, inasmuch as the use of n-butyllithium involves the formation of 10-n-butyl-1,2-benzanthracene as a by product.

(III)

R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, iso-C_5H_{11}

This method of synthesizing the homologs of 1,2-benzanthracene, of which 10-methyl-1,2-benzanthracene is a highly active carcinogenic agent in animals, as strong as cholanthrene, is superior to all the methods suggested up to now for the synthesis of these hydrocarbons in simplicity and ease [2,3,4]. When 1,2-benzanthryl-10-lithium is reacted with ethyl chlorocarbonate, it is converted into the ethyl ester of 1,2-benzanthracene-10-carboxylic acid (IV); reacting compound (I) with ethylene oxide yields 10-β-oxethyl-1,2-benzanthracene (V), with a yield that is 77% of the theoretical. The latter compound was synthesized by Badger and Cook [5] with a yield of 29% by reacting ethylene oxide with the organomagnesium compound of 1,2-benzanthracene, which was synthesized with great difficulty.

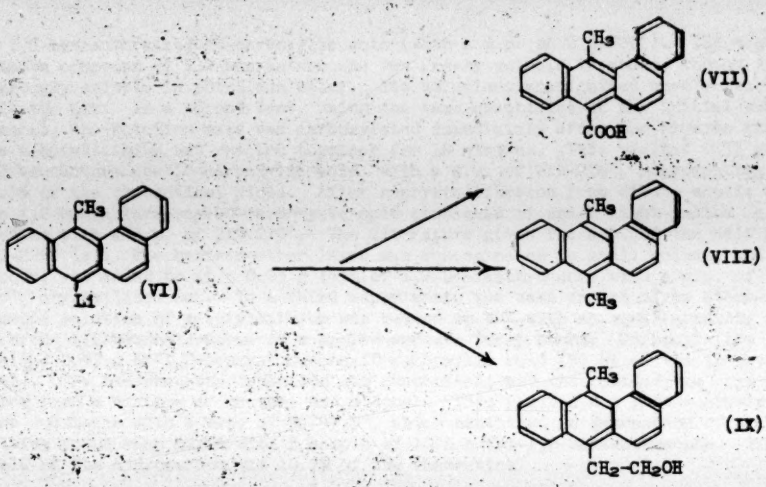
(IV) (V)

When we react the organolithium compound (I) with acetophenone we get 1,2-benzanthracene instead of an addition product.

9-Methyl-10-bromo-1,2-benzanthracene reacts with n-butyllithium like 10-bromo-1,2-benzanthracene. The resultant 9-methyl-1,2-benzanthryl-10-lithium (VI) is converted into 9-methyl-1,2-benzanthracene-10-carboxylic acid (VII) by the action of carbon dioxide; the organolithium compound (VI) reacts with methyl iodide to yield 9,10-dimethyl-1,2-benzanthracene (VIII), which is an extremely strong carcinogenic hydrocarbon. Reacting (VI) with ethylene oxide yields 9-methyl-10-β-oxethyl-1,2-benzanthracene (IX) (See following page).

EXPERIMENTAL

All operations with organolithium compounds were performed in an atmosphere of anhydrous nitrogen.



Action of lithium on 10-bromo-1,2-benzanthracene. a) In ether. 0.5 g of pulverized 10-bromo-1,2-benzanthracene (m.p. 151.0-151.5°), 20 ml of absolute ether, and 0.05 g of finely cut metallic lithium were sealed in an ampoule, which was heated to 45° with periodic shakings. The reaction set in after 1.5 hours had elapsed, isolated red spots appearing on the surface of the metal. Two hours after the onset of the reaction the deposit of 10-bromo-1,2-benzanthracene had vanished. The deep-crimson reaction mixture was poured over pulverized solid carbon dioxide; water and benzene were added to the reaction products, the aqueous layer being separated and acidulated with dilute hydrochloric acid. This yielded 0.03 g of 1,2-benzanthracene-10-carboxylic acid (6.8% of the theoretical), with a m.p. of 218-220° after recrystallization. The benzene solution yielded 0.2 g of 1,2-benzanthracene with a m.p. of 157-160°, representing a 54% yield. This procedure involving carboxylation and subsequent isolation of the reaction products was employed in the subsequent tests.

b) In an ether-benzene mixture. An ether benzene solution (1:1, 14 ml) of 0.5 g of 10-bromo-1,2-benzanthracene and 0.05 g of finely cut lithium was heated in a sealed ampoule to 40-45°. The reaction mixture turned red after 20 minutes of heating. After an hour of heating, the dark-purple solution was carboxylated. The reaction products yielded 0.16 g of 1,2-benzanthracene-10-carboxylic acid, with a m.p. of 210-221° (36.4% of the theoretical), and 0.08 g of 1,2-benzanthracene (21.6% of the theoretical).

Action of n-butyllithium upon 10-bromo-1,2-benzanthracene. 0.5 g of n-butyl chloride, 15 ml of absolute ether, and 0.1 g of lithium cut into thin leaflets were sealed into a Schlenk tube, and the tube was agitated for 2 hours. The resulting solution of n-butyllithium was filtered through a No. 4 glass filter to remove the excess lithium and the lithium chloride, and 1 g of 10-bromo-1,2-benzanthracene, dissolved in 15 ml of anhydrous benzene (containing no thiophene), was added to the filtrate. The reaction mass was agitated for 10 minutes, and then part of the ether was driven off in vacuum. The chilled solution yielded a finely crystalline yellow precipitate of 1,2-benzanthryl-10-lithium, which was filtered out, dissolved in ether, and carboxylated

to 1,2-benzanthracene-10-carboxylic acid (with a m.p. of 218-220°). The organolithium compound of 1,2-benzanthracene was freely soluble in ether, though very sparingly soluble in petroleum ether. Its solutions are ignited upon contact with the air. In a second test, using the same quantities of the initial substances, the reaction mass was carboxylated immediately after the bromide and the n-butyllithium had reacted together for 10 minutes. This yielded 0.73 g of 1,2-benzanthracene-10-carboxylic acid, with a m.p. of 212-216°, representing 82.3% of the theoretical yield. After recrystallization from dilute acetic acid, the 1,2-benzanthracene-10-carboxylic acid consisted of small light-yellow needles with a m.p. of 219-220°. The literature gives the m.p. of the acid as 219-220° [5]. The benzene-ether layer was concentrated to small volume, and alcohol was added to it. 0.03 g (4%) of 1,2-benzanthracene, with a m.p. of 159-160°, crystallized out. In a third experiment, the same amount of an ether-benzene solution of n-butyllithium was heated to 40° with an equal quantity of 10-bromo-1,2-benzanthracene in a sealed ampoule for 5 hours. Carboxylation yielded 0.47 g of 1,2-benzanthracene-10-carboxylic acid (52.8% of the theoretical). The benzene-ether solution was evaporated, and the residue was crystallized from a mixture of benzene and alcohol. This yielded 0.1 g of a crystalline substance with a m.p. of 96-97.5°, which exhibited no depression of the melting point when mixed with a sample of 10-n-butyl-1,2-benzanthracene. The yield of the hydrocarbon was 10.7% of the theoretical.

Action of phenyllithium on 10-bromo-1,2-benzanthracene. A solution of 1 g of 10-bromo-1,2-benzanthracene in 10 ml of benzene was added to a filtered ether solution of phenyllithium, prepared from 0.9 g of bromobenzene, 0.09 g of lithium, and 5 ml of absolute ether. The ampoule was then sealed and heated to 40° for 45 minutes, after which the cooled solution was carboxylated. This yielded 0.75 g of 1,2-benzanthracene-10-carboxylic acid, with a m.p. of 212-216°, the yield being 85% of the theoretical. We were unable to isolate a substance with individual properties from the ether-benzene solution. In a second experiment, made with the same amounts of the initial substances and run at 20° for 45 minutes, we secured 72.7% of the acid (0.64 g). The neutral fractions yielded 0.17 g of 10-bromo-1,2-benzanthracene. In a test that lasted 10 minutes at 20°, we got 45.4% of the acid (0.4 g) and 42% of the initial bromide (0.42 g). In tests lasting 2 and 5 hours at 40°, we secured 83.4% and 80% of the acid, respectively; the neutral fractions yielded 4 and 6.1%, respectively, of 1,2-benzanthracene.

10-Methyl-1,2-benzanthracene (III, R = CH_3). 3 g of 10-bromo-1,2-benzanthracene was added to a filtered solution of n-butyllithium, prepared from 1.5 g of n-butyl chloride. After the light-brown solution, which was chilled with ice water, had been agitated for 10 minutes, 4.2 g of methyl iodide, diluted with 15 ml of absolute ether, was added. The color of the reaction mixture turned light yellow. Two hours later the reaction mass was processed with water, and then the ether-benzene solution was evaporated to dryness. The residue was crystallized from a benzene-alcohol mixture. This yielded 1.89 g of a hydrocarbon as colorless needles with a m.p. of 137-139°, representing 80% of the theoretical yield. The hydrocarbon had a m.p. of 140-141° after being recrystallized once more. It exhibited no depression of the melting point when mixed with a sample of 10-methyl-1,2-benzanthracene prepared by the Fieser and Hershberg method [4].

10-Ethyl-1,2-benzanthracene (III, R = C_2H_5). a) Using n-butyllithium. An ether solution of 3 g of ethyl iodide was added to an organolithium compound of 1,2-benzanthracene, prepared from n-butyllithium and 2 g of 10-bromo-1,2-benzanthracene. The hermetically sealed container was heated to 50° for 3 hours. After having been washed with water, the ether-benzene layer was evaporated, and the residue was treated with 2 g of picric acid dissolved in benzene. The

precipitated picrate was twice crystallized from benzene. The hydrocarbon regenerated from the picrate was crystallized from ethyl alcohol. This yielded 0.79 g of a substance as light-yellow needles with a m.p. of 110-112°, representing 47.5% of the theoretical yield. It is difficult to purify this substance any further. The literature gives the m.p. of 10-ethyl-1,2-benzanthracene as 113.5-114° [4].

4.165 mg substance: 14.267 mg CO_2; 2.45 mg H_2O. Found %: C 93.48; H 6.49. $C_{20}H_{18}$. Computed %: C 93.71; H 6.29.

b) Using phenyllithium. 2 g of 10-bromo-1,2-benzanthracene, dissolved in 10 ml of anhydrous benzene, and 5 g of ethyl iodide, dissolved in 5 ml of absolute ether, were added to a filtered solution of phenyllithium, prepared from 1.8 g of bromobenzene, 0.18 g of finely cut metallic lithium, and 10 ml of absolute ether. The sealed ampoule was then heated to 40° for 3 hours. After the reaction mixture had been treated with water, the ether benzene layer was evaporated, and the residue was crystallized from petroleum ether. This yielded 1.28 g of a substance with a m.p. of 110-112°, or 77.1% of the theoretical yield. Recrystallization from the same solvent yielded 1.15 g (69.6% of the theoretical) of 10-ethyl-1,2-benzanthracene, with a m.p. of 113-114°.

10-n-Propyl-1,2-benzanthracene (III, R = n-C_3H_7. 1 g of 10-bromo-1,2-benzanthracene, dissolved in 10 ml of benzene, and 2.2 g of propyl iodide (prepared by the Dangyan method [6]) were sealed into an ampoule with an ether solution of phenyllithium (made from 0.9 g of bromobenzene). The sealed ampoule was heated to 40° for 3 hours, yielding 0.62 g or 70.4% of the theoretical of a hydrocarbon with a m.p. of 106-109°. Recrystallization from ethyl alcohol yielded 0.56 g of the hydrocarbon as slightly yellowish, tiny, fleecy needles, with a m.p. of 108.8-109.3°. The m.p. of 10-n-propyl-1,2-benzanthracene is given as 107-108° in the literature [4].

4.341 mg substance: 14.790 mg CO_2; 2.702 mg H_2O. Found %: C 92.98; H 6.96. $C_{21}H_{18}$. Computed %: C 93.29; H 6.71.

10-n-Butyl-1,2-benzanthracene (III, R = n-C_4H_9). a) A benzene solution of 1 g of 10-bromo-1,2-benzanthracene and an ether solution of 2.4 g of n-butyl iodide [6] were added to an ether solution of phenyllithium, prepared from 0.9 g of bromobenzene. The reaction mixture was heated to 40° for 3 hours, and then decomposed. Recrystallization of the residue from petroleum ether and then from ethyl alcohol yielded 0.6 g (64.6% of the theoretical) of a substance with a m.p. of 96.5-97.5°). The m.p. of 10-n-butyl-1,2-benzanthracene is given as 96.8-97.5° in the literature.

4.992 mg substance: 16.96 mg CO_2; 3.228 mg H_2O. Found %: C 92.72; H 7.23. $C_{22}H_{20}$. Computed %: C 92.95; H 7.04.

b) An ether solution of 1.34 g of n-butyl bromide was added to an organolithium compound, prepared from n-butyllithium and 1 g of 10-bromo-1,2-benzanthracene. The reaction mixture was heated to 40° for 3 hours. After the usual processing, the dry residue of the ether-benzene layer was recrystallized twice from petroleum ether, and then from ethyl alcohol.

This yielded 0.32 g of 10-n-butyl-1,2-benzanthracene, or 34.6% of the the theoretical, with a m.p. of 95-97°.

10-Isoamyl-1,2-benzanthracene (III, R = iso-C_5H_{11}). A benzene solution of 1 g of 10-bromo-1,2-benzanthracene and an ether solution of 3.9 g of isoamyl bromide [6] were sealed into an ampoule with an ether solution of phenyllithium, prepared from 0.9 g of bromobenzene. After the sealed ampoule had been heated to 40° for 3 hours, the reaction mixture was processed with water. Double

recrystallization of the ether-benzene layer's residue yielded 0.1 g of 1,2-benzanthracene. The evaporated mother liquor yielded a precipitate that was recrystallized from ethyl alcohol, yielding 0.46 g (47.2% of the theoretical) of a substance with a m.p. of 86.5-88°, as elongated, thin, colorless needles.

3.134 mg substance: 10.661 mg CO_2; 2.057 mg CO_2; Found %: C 92.83; H 7.34. $C_{23}H_{22}$. Computed %: C 92.58; H 7.42.

Action of acetophenone upon 1,2-benzanthryl-10-lithium. An ether solution of 0.45 g of acetophenone was added to an organolithium compound, prepared from n-butyllithium and 1 g of 10-bromo-1,2-benzanthracene. Thirty minutes later the reaction mixture was processed with water. The ether-benzene layer yielded 0.36 g (42.8%) of a crystalline product with a m.p. of 151-156°. This substance had a m.p. of 159-160° after recrystallization from petroleum ether and exhibited no depression of the melting point when mixed with a sample of 1,2-benzanthracene.

Ethyl ester of 1,2-benzanthracene-10-carboxylic acid (IV). 0.23 g of ethyl chlorocarbonate was added to a chilled ether-benzene solution of 1,2-benzanthracene-10-lithium, prepared as indicated above from n-butyllithium and 0.5 g of 10-bromo-1,2benzanthracene. Half an hour later the reaction mass was washed with water, the solvents were driven off, and the oily residue was crystallized from a mixture of benzene and petroleum ether. This yielded 0.28 g of a substance with a m.p. of 131-132.5°. The yield was 57% of the theoretical. Recrystallization of the ethyl ester of 1,2-benzanthracene-10-carboxylic acid yielded small light-yellow prisms with a m.p. of 132-133.5°.

4.443 mg substance: 13.680 mg CO_2; 2.141 mg H_2O. Found %: C 84.02; H 5.39. $C_{21}H_{18}O_2$. Computed %: C 83.97; H 5.37.

10-β-Oxethyl-1,2-benzanthracene (V). Gaseous ethylene oxide (about 1 g) was passed through a solution of an organolithium compound, prepared from n-butyllithium and 1 g of 10-bromo-1,2-benzanthracene. The mixture warmed up, and a voluminous amorphous precipitate of the alcoholate was thrown down. When the reaction was over, the lithium alcoholate was decomposed with water, and the resulting precipitate was filtered out, yielding 0.51 g of 10-β-oxethyl-1,2-benzanthracene with a m.p. of 182-184°.

The residue left after the solvents had been driven off was crystallized from benzene, yielding 0.24 g of a substance with a m.p. of 180-183°. The yield of the 10-β-oxethyl-1,2-benzanthracene was 85.2% of the theoretical. Recrystallization from ethyl alcohol yielded 0.68 g of white, small, fleecy needles with a m.p. of 186.7-187.5°. The m.p. of 10-β-oxethyl-1,2-benzanthracene is given in the literature as 181.5-182.5°, [5].

3.828 mg substance: 12.339 mg CO_2; 2.034 mg H_2O. Found %: C 87.96; H 5.94. $C_{20}H_{16}O$. Computed %: C 88.20; H 5.92.

9-Methyl-1,2-benzanthracene-10-carboxylic acid (VII). A solution of 1 g of 9-methyl-10-bromo-1,2-benzanthracene in 20 ml of benzene was added to a filtered ether solution of n-butyllithium, prepared as indicated above from 0.5 g of n-butyl chloride, 0.1 g of lithium, and 20 ml of absolute ether. Ten minutes later the reaction mass was poured over solid carbon dioxide. Then it was treated with water, and the filtered aqueous layer was acidulated, yielding 0.34 g of acid, or 38.2% of the theoretical yield. Recrystallization from ethyl alcohol yielded the 9-methyl-1,2-benzanthracene-10-carboxylic acid as minute, light-yellow needles, with a m.p. of 224.5-228° (with decomposition).

3.587 mg substance: 11.062 mg CO_2; 1.627 mg H_2O. Found %: C 84.16; H 5.07. $C_{20}H_{14}O_2$. Computed %: C 83.89; H 4.93.

9,10-Dimethyl-1,2-benzanthracene (VIII). 1.3 g of methyl iodide was added to an ether-benzene solution of 9-methyl-1,2-benzanthryl-10-lithium, prepared from 1 g of 9-methyl-10-bromo-1,2-benzanthracene. A small quantity of heat was evolved during the reaction, and the color of the solution turned light yellow. Two hours later the reaction mass was washed with water, and the ether-benzene layer was evaporated to dryness. The residue was crystallized twice from ethyl alcohol, yielding 0.5 g of a hydrocarbon as light-yellow leaflets, representing 62.5% of the theoretical yield. This substance exhibited no depression of the melting point when mixed with a sample of 9,10-dimethyl-1,2-benzanthracene that we had prepared by another method [7].

9-Methyl-10-β-oxethyl-1,2-benzanthracene (IX). The initial reagents were used in the same quantities as in the preceding test. Passing 1 g of ethylene oxide through the ice-chilled solution of the organolithium compound resulted in the throwing down of an amorphous precipitate. Twenty minutes later the lithium alcoholate was decomposed with water, the ether-benzene layer was separated, and the solvents were driven off. The residue was crystallized from benzene, yielding 0.57 g of a substance with a m.p. of 135-138°, a yield that was 64% of the theoretical. Recrystallizations from ethyl alcohol and acetone yielded the 9-methyl-10-β-oxethyl-1,2-benzanthracene as slightly yellowish, minute needles with a m.p. of 138-140°.

4.316 mg substance: 13.886 mg CO_2; 2.531 mg H_2O. Found %: C 87.80. H 6.56. $C_{21}H_{18}O$. Computed %: C 88.07; H 6.34.

SUMMARY

1. The method of synthesizing organolithium compounds based upon the reaction of lithium with halogen derivatives cannot be employed in the 1,2-benzanthracenes.

2. Organolithium compounds of the 1,2-benzanthracenes can be readily prepared by reacting n-butyllithium or phenyllithium with halogen derivatives of the hydrocarbons.

3. Organolithium derivatives may be successfully employed in synthesizing the homologs and oxygen derivatives of 1,2-benzanthracene.

4. The synthesis of 10-ethyl-1,2-benzanthracene and its higher homologs requires the preparation of 1,2-benzanthryl-10-lithium from phenyllithium.

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THE REACTION OF SOME ORGANOMERCURY COMPOUNDS WITH SUCCININIDE

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The bond between mercury and carbon is a rather stable one. Complete organomercury compounds do not react with water, ammonia, and alcohols. Many instances are known, however, of the detachment of radicals from these compounds by acids, sulfides, halides, hydrohalides, metallic halides and cyanides, phosphorus halides, acid halides, metals [1], phenols [2], hydrogen [3], ultraviolet light [4], etc.

The reaction of succinimide with complete organomercury compounds has not been described up to now, as far as we know. We investigated the reactions of succinimide with the following complete organomercury compounds: diphenylmercury, o-ditolylmercury, diethylmercury, dibenzylmercury, and α- and β-dinaphthylmercury. These reactions have yielded: phenylmercurysuccinimide, o-tolylmercurysuccinimide, ethylmercurysuccinimide, and α- and β-naphthylmercurysuccinimide, respectively. No mercurysuccinimide was formed with dibenzylmercury, the reaction yielding only metallic mercury and dibenzyl. The R-mercurysuccinimides are well-shaped crystals, for the most part very freely soluble in hot water, benzene, and chloroform. The structure of the synthesized R-mercurysuccinimides was confirmed by analysis for mercury, as well as by their reactions with hydrochloric acid, which was quantitative in accordance with the following equation:

$$RHgN(COCH_2)_2 + HCl \longrightarrow RHgCl + HN(COCH_2)_2,$$

and by synthesis from phenylmercury hydroxide and succinimide.

Only one derivative is described in the literature, the ArHg radical being attached to the nitrogen atom in the succinimide, viz.: p-hydroxyphenylmercurysuccinimide. It was synthesized by reacting p-hydroxyphenylmercury chloride with succinimide in an alkaline alcoholic solution [5]. We also possess some patent information on syntheses of various derivatives from ArHgOH and ArHgOCOCH$_3$ by reacting them with succinimide, phthalimide, pyrrole, piperidine, secondary amines, and other nitrogen compounds [6]. No individual substances have been described, however.

Reacting hydrogen sulfide with phenyl- and o-tolylmercurysuccinimides yields complete organomercury compounds. The ethyl- and α-naphthylmercurysuccinimides yield the respective $(RHg)_2S$ sulfides. RHgI is formed with potassium iodide:

$$RHgN(COCH_2)_2 + KI \longrightarrow RHgI + (CH_2CO)_2NK.$$

Thus the reaction of complete organomercury compounds with succinimide is quite general. This reaction may be used to convert the usually rather difficultly soluble R_2Hg into the freely soluble compounds (even in water) of the $RHgN(COCH_2)_2$ type, which in turn readily yield other derivatives of the RHgX type. The reaction is free from tarring or the formation of by-products and may be employed for the synthesis of mercury preparations that are readily soluble in

water and for establishing the structure of organomercury compounds.

EXPERIMENTAL

Reaction of organomercury compounds with succinimide. The organomercury compounds were reacted with succinimide in a reaction vessel heated over an oil bath. The reagents were reacted together in the molten state. In the high-melting organomercury compounds (α- and β-dinaphthylmercury) the succinimide, used in excess, acted as a solvent. Our experimental results are tabulated in the subjoined Table 1.

TABLE 1

Test No.	R_2Hg	Used for the reaction, grams		Oil-bath temperature, °	RH Yield	$RHGN(COCH_2)_2$ yield
		R_2Hg	$HN(COCH_2)_2$		%	%
1	$(C_6H_5)_2Hg$	3.5	2.0	135-140°	77.9	90.4
2	$(o\text{-}CH_3C_6H_4)_2Hg$	1.2	1.2	155.165	89.6	83.7
3	$(C_6H_5CH_2)_2Hg$.	3.8	1.0	150-160	-	-
4	$(C_2H_5)_2Hg$	4.9	3.0	135-145	96.6	86.9
5	$(\alpha\text{-}C_{10}H_7)_2Hg$..	2.3	1.0	140-145	64.6	63.2
6	$(\beta\text{-}C_{10}H_7)_2Hg$..	2.3	1.0	145-155	100.0	57.1

Tests 1, 2, and 3 were run in a round-bottomed flask for distilling solid substances, with a sword-shaped side tube, to which a small reflux condenser was attached.

In Tests 1 and 2 the respective aromatic hydrocarbons were condensed in the side tube. They were determined by synthesizing their nitro derivatives: the benzene was nitrated to m-dinitrobenzene (m.p. 90°), and the toluene to 2,4-dinitrotoluene (m.p. 70°). These latter compounds exhibited no depression when mixed with the pure products. No toluene was found in Test 3. Mercury was precipitated during the reaction. The contents of the flask were dissolved in a acetone, and the mercury was filtered out. The mercury weighed 1.9 g, or 96.5% of the theoretical. The acetone was driven out of the filtrate, and the residue was steam-distilled, 1.6 g (88%) of dibenzyl with a m.p. of 52° being distilled off; it exhibited no depression when mixed with the pure substance. Test 4 was run in a round-bottomed flask fitted with a reflux condenser connected to a gas buret. A total of 440 ml (0.6 g) of ethane was evolved. The ethane was measured by burning it in the All-Union Heat Engineering Institute apparatus, the experimental data being as follows: active gas used: 6.10 ml; gas volume after combustion: 13.00 ml; gas volume after absorption by alkali: 0.25 ml; CO_2 volume: 12.75 ml. There were no unsaturated hydrocarbons. Tests 5 and 6 were run in a large test tube. Naphthalene began to sublime during the reaction. The melt was distilled with steam, yielding naphthalene, with a m.p. of 80°. The organomercury derivatives of succinimide were extracted from the reaction vessel with water in all the experiments except Test 4, the pure products being recovered by an ensuing double recrystallization from water. The excess succinimide reamined in the mother liquor.

Ethylmercurysuccinimide (Test 4) is very freely soluble in cold water, so that it could not be freed of its excess succinimide by recrystallization from water. The melt in the reaction flask was extracted with hot dichloroethane, the succinimide settling out as the solution cooled. The succinimide was filtered out, and the filtrate evaporated, the precipitated ethylmercury succinimide being recrystallized twice from CCl_4. This yielded a pure product. The

properties of the organomercury derivatives of succinimide are summarized in Table 2.

TABLE 2

Test No.	$RHgN(COCH_2)_2$	Melting point, °C	Solubility				Appearance of crystals (from H_2O)
			In cold water	In hot water	In CCl_4	In hot benzene	
1	$C_6H_5HgN(COCH_2)_2$.....	192-193	Low	High	Low	High	Colorless needles
2	$o\text{-}CH_3C_6H_4HgN(COCH_2)_2$	178	Low	High	Low	High	Colorless leaflets
3	$C_2H_5HgN(COCH_2)_2$.....	121-123	Very high	Very high	High	Very high	
4	$\alpha\text{-}C_{10}H_7HgN(COCH_2)_2$..	183	Poor	Low	Low	High	
5	$\beta\text{-}C_{10}H_7HgN(COCH_2)$...	220-222	Poor	Low	Low	High	

We made a quantitative analysis of the mercury in these substances. A weighed sample of the $RHgN(COCH_2)_2$ was burned with a mixture of nitric and sulfuric acids, the mercury cation being precipitated with hydrogen sulfide. The analysis results are listed in Table 3.

TABLE 3

Test No.	$RHgN(COCH_2)_2$	Weight, grams	HgS produced, grams	Per cent mercury	
				Experimental	Calculated
1	$C_6H_5HgN(COCH_2)_2$.....	0.3699	0.2287	53.31	53.40
2	$o\text{-}CH_3C_6H_4HgN(COCH_2)_2$...	0.3169	0.1883	51.21	51.49
3	$C_2H_5HgN(COCH_2)_2$.....	0.2864	0.2020	60.83	61.23
4	$\alpha\text{-}C_{10}H_7HgN(COCH_2)_2$.....	0.2491	0.1356	46.96	47.13
5	$\beta\text{-}C_{10}H_7HgN(COCH_2)_2$.....	0.2113	0.1140	46.51	47.13

Reaction of $RHgN(COCH_2)_2$ with HCl, KI, and H_2S. These reactions were carried out in test tubes. The amount of $RHgN(COCH_2)_2$ used ranged from 0.2 to 1.0 g. The solvent for the ethylmercury succinimide was water, a water-alcohol mixture being used for the other succinimide derivatives. The solutions were heated to 70-80°. An excess of potassium iodide, amounting to ten times the required quantity, was employed. The reactions with HCl and KI were instantaneous, white precipitates being thrown down. After the mixtures had stood for a short while, the precipitates were filtered out, washed with water, dried, and twice recrystallized from hot acetone or benzene. When H_2S was passed through the solutions of $C_6H_5HgN(COCH_2)_2$ and $o\text{-}CH_3C_6H_4HgN(COCH_2)_2$, white sulfides were formed at first, being subsequently decomposed into grayish-black products by the addition of more H_2S. The mixtures were boiled for 15 minutes, and then the precipitates were filtered out, washed with hot water, and dried. The diphenylmercury and o-ditolylmercury were extracted with hot benzene. Diphenylmercury had a m.p. of 125°, and o-ditolylmercury a m.p. of 107°, neither compound exhibiting any depression when mixed with the pure substance.

Sulfides were precipited in the reactions of $C_2H_5HgN(COCH_2)_2$ and $\alpha\text{-}C_{10}H_7HgN(COCH_2)_2$ with H_2S. In every instance the reaction products were identified by their melting points and fusion tests of samples mixed with the pure substances. The following organomercury products were obtained in the reactions with HCl and KI, (Table 4).

TABLE 4

Test No.	$RHgN(COCH_2)_2$	Reaction with HCl				Reaction with KI			
		Reaction product	grams of initial product used	% yield	M.p. of product	Reaction product	grams of initial product used	% yield	M.p. of product
1	$C_6H_5HgN(COCH_2)_2$.....	C_6H_5HgCl.....	1.05	98	251°	C_6H_5HgI.....	0.30	94	266°
2	$o\text{-}CH_3C_6H_4HgN(COCH_2)_2$	$o\text{-}CH_3C_6H_4HgCl$	–	–	146	$o\text{-}CH_3C_6H_4HgI$	–	–	174
3	$C_2H_5HgN(COCH_2)_2$.....	C_2H_5HgCl.....	1.10	95	193	C_2H_5HgI.....	0.20	91	186
4	$\alpha\text{-}C_{10}H_7HgN(COCH_2)_2$..	$\alpha\text{-}C_{10}H_7HgCl$..	0.31	77	189	$\alpha\text{-}C_{10}H_7HgI$..	0.30	69	185
5	$\beta\text{-}C_{10}H_7HgN(COCH_2)_2$..	$\beta\text{-}C_{10}H_7HgCl$..	–	–	266	–	–	–	–

SUMMARY

1. A study has been made of the reactions of succinimide with diphenylmercury, o-ditolylmercury, diethylmercury, α-dinaphthylmercury, and β-dinaphthylmercury. It has been demonstrated that $RHgN(COCH_2)_2$ is formed in every case.

2. All the organomercury derivatives of succinimide of the $RHgN(COCH_2)_2$ type have been synthesized for the first time; they are readily crystallizable colorless substances that are soluble in water.

3. When reacted with hydrochloric acid or potassium chloride, all these compounds yield the respective chlorides and iodides, their general formula being RHgX. Phenylmercurysuccinimide and o-tolylmercurysuccinimide yield diphenylmercury and o-ditolylmercury, respectively, when reacted with hydrogen sulfide, whereas α-naphthylmercurysuccinimide and ethylmercurysuccinimide yield sulfides of the $(RHg)_2S$ type.

4. Reacting dibenzylmercury with succinimide yields dibenzyl and mercury.

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THE STRUCTURE OF BISULFITE DERIVATIVES OF THE AROMATIC COMPOUNDS

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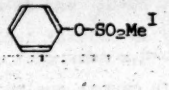
As we know, the ability to form bisulfite derivatives is characteristic of a large number of aromatic compounds, viz.: individual representatives of the naphtholsulfonic acids, naphthol- and aminoazo dyes, nitroso- and aminophthols, quinones, polyatomic phenols, and benzeneazo-benzenehydrazonaphthalenes. Several views have been put forward in the literature concerning the structure and the mechanism of the formation of bisulfite derivatives of this sort.* In the earliest papers (G.Bucherer, A. Spiegel), some of them were assigned the structure of Type (I) or (II). Later, it was supposed that only the ketone forms of the enumerated aromatic compounds could react with bisulfites, forming bisulfite compounds of Type (III), according to some researchers, and α-hydroxy sulfo acids of Type (IV), according to others (N.N.Vorozhtsov, sr., W.Fuchs, A.D.Lebedev, and V.N.Ufimtsev). S.V.Bogdanov believes that these ketone forms add a molecule of the bisulfite at the $\rangle C{=}C\langle$ double bond of the ring, yielding bisulfite compounds of Type (V)



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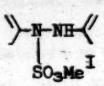

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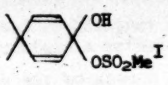

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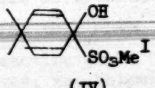

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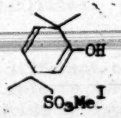

(V)

This indicates how the views of the research workers in the field differ concerning the structure of these bisulfite compounds. As the result of the researches of Vorozhtsov, Sr., Bogdanov, and Ufimtsev, it may be regarded as proved, to be sure, that these compounds do not have Type (I) structures. There is evdence that at least some of them do not possess Type (II) structures. As for the other types of structural formulas, none of them has yet been established experimentally to the point where it may be regarded as beyond cavil. The reasons for this are as follows: the instability of the intermediate reaction products and, in some instances, of the final bisulfite compounds as well; our not possessing effective methods for isolating them, which would guarantee that the substances do not change during the refining process; and the lack of reliable

* The literature on this problem is largely summarized in the papers [1-14].

methods for proving the nature and the position of the substituents in the molecules of the bisulfite compounds. All this forces us to approach new assertions, and, even more so, generalizations concerning the structure of substances of this kind with great caution.

Several experimental papers have been published during recent years by Ufimtsev [1-13], in which he states that all bisulfite compounds, without exception, have the Type (IV) structure. In these papers he rejects all other views expressed in the literature, while proposing a series of new equations to explain the way in which bisulfite compounds are formed and their subsequent transformations. These papers of Ufimtsev's give the impression that the problem of the structure of bisulfite compounds, which has been a moot point for so long, has at last been solved once and for all. We have pointed out in previous papers [15-21], however, that Ufimtsev's notions are wrong as far as the bisulfite compounds of paraquinones are concerned. A consideration of Ufimtsev's researches, and in some instances an experimental check, involving the structure of bisulfite compounds of other types of derivatives of aromatic compounds,* likewise led us to conclude that his research methods, his manner of proving the structure of the substances, and the course of his reasoning were all far from convincing.

Let us begin with Ufimtsev's assertion that all the derivatives of aromatic compounds he had tested [1-13], reacting in their ketonic form, added a bisulfite molecule at the double bond of the carbonyl group, forming α-hydroxy sulfo acids, the structure of which was that of the usual bisulfite compounds of aldehydes and ketones [Type (IV) formulas]. In this connection, two very well-known circumstances must be pointed out: 1) that the $\rangle C{=}O$ group of ketones can react with bisulfites whenever it is directly attached to at least one methyl or two methylene groups; 2) that the bisulfite molecule is usually added to α,β-unsaturated ketones at the $\rangle C{=}C\langle$ double bond rather than at the $C{=}O$. It follows, therefore, that insofar as the aromatic compounds investigated by Ufimtsev in their ketonic form were α,β-unsaturated ketones and did not contain a methyl group or two methylene groups attached to the $\rangle C{=}O$ group, there was no ground for supposing that these compounds had to be converted into the respective α-hydroxy sulfo acids as the result of their reactions with bisulfites. On the contrary, it had to be assumed that the $\rangle C{=}C\langle$ bond of the ring would react with the bisulfites or that the reaction would follow a wholly different course.** Indeed, no one (not even Ufimtsev, see below) has ever been able to submit rigorous proof that these bisulfite compounds are α-hydroxy sulfo acids of Type (IV).

In fact, what are the research methods underlying the attribution of the structure of α-hydroxy sulfo acids to these bisulfite compounds? As for the general methods (in some instances the only methods employed by Ufmitsev and others***), they consist solely of determining the empirical formulas of the isolated bisulfite compounds and their decomposition into their initial constituents by alkalies or acids, the latter reaction being regarded as proof of the correctness of the Type (IV) formulas, since the ordinary bisulfite compounds of

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*Namely, naphtholsulfo acids, naphthol and amino azo dyes, nitroso- and aminonaphthols, benzeneazo- benzenehydrazonaphthalenes, and polyatomic phenols (resorcinol) [1-13].

**Except for the ketonic forms of some polyatomic phenols (resorcinol), which add bisulfite at the $\rangle C{=}C\langle$ and the $\rangle C{=}O$ double-bonds owing to their having two methylene groups. It is obvious that this is further confirmation of our comments (also vide infra).

***For example in the study of the bisulfite compounds of naphtholsulfo acids and amino azo dyes [5,7,11,18, 22,23] and of the bisulfite compound of the α-methyl-α-phenylhydrazone of 1,4-naphthoquinone [12].

aldehydes and ketones possess similar properties. It is obvious, however, that a method involving the detaching of the groups that had been previously attached to the initial molecule cannot be regarded as a rigid proof of the nature and the position of the substituents in the molecule formed. Moreover, the following facts are ignored entirely: 1) the difference between the Type (II), (III), (IV), and (V) formulas, all of which represent the same ultimate analysis, lies precisely in the nature and position of the substituent groups; 2) we still have no substantial proof of any difference in the behavior of Type (IV) and (V) bisulfite compounds with acid and alkali solutions.*

Therefore, these general research methods cannot be regarded as proof of the correctness of any of these formulas. Hence, the assertion of Ufimtsev and other researchers that the types of bisulfite compounds they had investigated were α-hydroxy sulfo acids, with the general formula (IV), is merely a hypothesis. Nor does this hypothesis appear any more convincing after a critical analysis of the special methods described by Ufimtsev for demonstrating the structure of bisulfite compounds. We shall deal with these methods briefly below.

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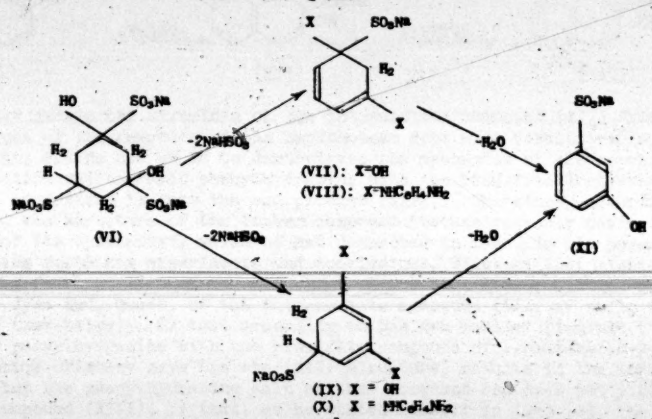
*In this connection we may refer to Ufimtsev's unfounded assertion that only those bisulfite molecules that are added at the $>C=O$ double bond [Type (IV)] are readily split off in the presence of an alkali, but not those attached to the $>C=C<$ [Type (V)] [10]. Ufimtsev made this statement after making a study of the properties of the bisulfite derivative of resorcinol (VI), the molecule of which represents both types, (IV) and (V).

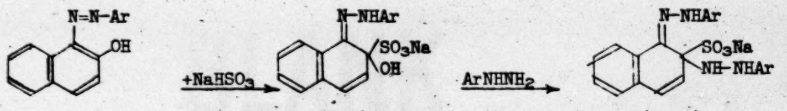
We know [26] that an alkali can convert the compound (VI) into (XI), either by (VI) → (VII) → (XI) or by the equally probable reactions (VI) → (IX) → (XI):



Isolating the intermediate compound [(VII) or (IX)] as a p-phenylenediamine derivative, but failing to demonstrate the position of the substituents in the latter's ring [10], Ufimtsev arbitrarily assigned it the structure of (X), whence he assumed that the reaction sequence (VI) → (IX) → (XI) was proved and then inferred that the alkali split off those bisulfite molecules that were attached to the $>C=O$ double bond rather than to the $>C=C<$. But, inasmuch as the formation of the compounds (VII) or (IX) is equally probable *a priori*, while both of them can form the respective isomeric derivatives (VIII) and (IX) equally easily, the question of which of these two compounds is actually formed can be decided only by ascertaining the position of the substituents in the isolated p-phenylenediamine derivative. It is therefore obvious that, not having solved this problem, Ufimtsev had no right to assert that this derivative had the (X) structure; all his subsequent inferences are therefore equally groundless.

1. Let us consider the method used by Ufimtsev to demonstrate the structure of the bisulfite compounds of naphtholazo dyes [3]. This method was designed to prove that the Type (IV) formula was correct and that the Type (V) formula was incorrect. The only difference between the two is the position of the sulfo groups and the double bonds in the ring. Hence, proving the position of the sulfo groups, say, would decide the problem of which formula was right. The method described by Ufimtsev, however, was as follows: the bisulfite compound of the naphtholazo dye was first reduced cautiously, and then subjected to a stiff hydrolysis (cf [3], pp. 375-376, Experiment 6), resulting in the detaching of the sulfo group from the molecule. It is obvious that recovering a substance deprived of its sulfo group as the sole product of these transformations in no way solves the problem of the position of this group in the initial molecule. Ufimtsev believes [3], however, that this very method enables him to determine the position of the sulfo group in molecules of the bisulfite compounds of naphtholazo dyes and to demonstrate that the structure of these compounds is represented by Type (IV) formulas, and not by Type (V). The groundlessness of these assertions needs no further explanation.*

2. Ufimtsev used another approach to demonstrate the structure and the mechanism of formation of the bisulfite compounds of benzeneazo-benzenehydrazonaphthalenes. He believes that the latter are formed as follows from o-naphtholazo dyes [3].**



(XII) (XIII)

Ufimtsev judges the structure of the intermediate compound (XII) from his investigations of the reaction of the naphtholazo dyes with bisulfites [2,3]. As he sees it, all he had to do to demonstrate the mechanism of the second stage of this reaction was to react phenylhydrazine with the bisulfite derivative (XII), thus converting it into the end product (XIII). Therefore, according to Ufimtsev, the structure of the latter compound "is unmistakably defined by the method of its synthesis", which he had described in 1946, in his paper [3]. But in setting forth his experiments and conclusions, Ufimtsev lost sight of the following factors: 1) that the structure of the bisulfite compounds of naphtholazo dyes and, hence, of the intermediate compound (XII) as well, is far from proved (see below); 2) that according to his own earlier findings [3], the reaction of phenylhydrazine with the bisulfite compound of 1-benzeneazo-2-naphthol [which Ufimtsev says has the (XII) structure] results in the formation of nothing but the phenylhydrazine salt of this compound and does not yield the bisulfite compound (XIII); 3) that, as he stated himself in 1943 [3], the reaction resulting in the formation of a bisulfite compound of 1-benzeneazo-2-benzenehydrazonaphthalene cannot take place along the lines set forth above, since this reaction "by no means involves the direct reaction of the bisulfite compound (XII) with phenylhydrazine, but is much more complicated", requiring an excess of bisulfite in addition to the presence of phenylhydrazine (cf [3], p.

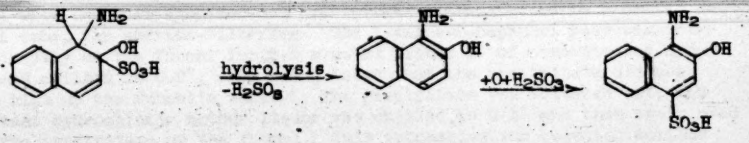
* Nor are the absorption curves given by Ufimtsev and Levin [2] for the bisulfite compounds of naphtholazo dyes evidence of the correctness of the Type (IV) formula, since these curves do not allow us to draw any definite conclusions as to the structure of the substances in question.

** Ufimtsev cites a similar reaction for the p-naphtholazo dyes [3].

370); and 4) that the new experimental findings he describes himself [9] serve to confirm the standpoint he had expressed previously [3], rather than his new reaction scheme, set forth above. In fact, instead of reacting nothing but phenylhydrazine with the bisulfite compound of 1-benzeneazo-2-(as well as 4-)-naphthol (as Ufimtsev's second set of reactions calls for), he carried out this reaction with bisulfite as well as phenylhydrazine present, while the synthesis of his end product required the heating of the isolated intermediate product with benzaldehyde [9]. It is clear that the conditions in which Ufimtsev managed to carry out this process have nothing in common with the conditions required for proving the correctness of the set of reactions he suggests, while the new experiments he describes merely bear out his earlier point of view concerning the incorrectness of this reaction set and, hence, of Formula (XII) as well.

3. In conclusion, we must take up three methods of research that enabled Ufimtsev to assert that the bisulfite compound of 1-nitroso-2-naphthol possesses the Type (IV) structure. These investigations boil down to the following [4]. Reducing the bisulfite compound of 1-nitroso-2-naphthol under mild conditions, Ufimtsev assigned the structure of the bisulfite compound of 1-amino-2-naphthol (XIV) to the reduction product he had isolated, then held that, like the latter, the initial bisulfite compound of 1-nitroso-2-naphthol must also have the Type (IV) structure. Ufimtsev cites the following findings in support of the structural formula (XIV) for the bisulfite compound of 1-amino-2-naphthol [4]: its empirical formula, its ability to be decomposed to 1-amino-2-naphthol when acted upon by an alkali or an acid, and, lastly, the fact that it can be oxidized in an aqueous solution in the cold by atmospheric oxygen to 1-amino-2-naphthol-4-sulfonic acid (XVI). The first two facts, however, give absolutely no indication of the position of the sulfo group in the molecules of the bisulfite compounds of either 1-amino- or 1-nitroso-2-naphthol, whereas the last fact indicates that the sulfo group is located at the 4 position instead of the 2 position. There is, therefore, no reason to believe that these bisulfite compounds possess the Type (IV) structure; on the contrary, it is very likely that their structure is that of Type (V), as asserted by Bogdanov [24].*

There is one more problem discussed by Ufimtsev that we must take up. Adopting the structure (XIV) for the bisulfite compound of 1-amino-2-naphthol he had described and finding that the latter can be oxidized to the sulfo acid (XVI) under the conditions set forth above, Ufimtsev proposed the following set of reactions to explain these transformations [4]:



(XIV) (XV) (XVI)

According to Ufimtsev, this set of reactions was checked by him experimentally. But when we reviewed the experiments in question (cf [4], pp. 162-163), we found that they were performed under conditions that bore no resemblance to those of his basic experiment involving the oxidation of the compound (XIV) to

* In an effort to make a closer investigation of the structure of the bisulfite compound of 1-amino-2-naphthol described by Ufimtsev, we tried to synthesize this compound and then study its transformations. We were unable to reproduce the synthesis of this substance, however, either under the conditions specified by Ufimtsev [4] or after making some modifications of this method. In every case we recovered nothing but 1-amino-4-naphthol 4-sulfonic acid and 1-amino-2-naphthol.

the sulfo acid (XVI). This comparison forced us to doubt the correctness of Ufimtsev's sequence, which seemed to us to be unlikely in general, inasmuch as the intermediate 1-amino-2-naphthol (XV) had to be sulfonated at room temperature by an approximately 1% aqueous solution of H_2SO_3 or H_2SO_4, according to the conditions he described.

We therefore thought it advisable to go into this matter somewhat deeper, studying the ability of 1-amino-2-naphthol (XV) to be sulfonated to the sulfo acid (XVI) under the conditions called for by Ufimtsev's diagram. As was to be expected, however, 1-amino-2-naphthol underwent no changes at all under these conditions (cf the experimental section below). Hence, both the Ufimtsev diagram cited above and his assertion that he had verified this diagram experimentally had to be rejected as false.

We must therefore conclude that the experimental data available in the literature do not enable us as yet to adopt either one of the structural formulas advanced for the bisulfite derivatives of aromatic compounds as the correct one.

EXPERIMENTAL

To investigate the feasibility of sulfonating 1-amino-2-naphthol by dilute solutions of sulfuric or sulfurous acids (in the latter case with atmospheric oxygen present), we first had to find a way of recovering 1-amino-2-naphthol quantitatively from dilute solutions of its salts, and then determining it with a sufficiently high degree of accuracy. This method, developed by us, is set forth below.

1. Determination of 1-amino-2-naphthol. 1.00 g of freshly recrystallized 1-amino-2-naphthol hydrochloride, dried to constant weight at 30-40° in vacuum, was dissolved at 20° in 50 ml of a 0.1% solution of sulfurous acid. An aqueous solution of 2 g of sodium acetate trihydrate saturated in the cold was added to the resulting solution. A white precipitate of the 1-amino-2-naphthol base was thrown down at once. The resultant mixture was chilled to 0-2°, and the precipitate was filtered out on a weighed Schott No. 3 funnel. The precipitate was quantitatively transferred to the funnel by means of the mother liquor, care being taken that the precipitate was always covered by a layer of the liquid. After all the 1-amino-2-naphthol had been transferred to the funnel, it was squeezed out and then washed five times with a 0.01% aqueous solution of sulfurous acid chilled to 0-5°, with 5-6 ml of the solution used each time. Then the funnel with the well-squeezed-out precipitate was connected to a small, 8-10 ml test tube, for suction-filtering. The 1-amino-2-naphthol base was triturated directly on the funnel for 5-8 minutes with 5 ml of concentrated hydrochloric acid chilled to 0-2°, care being taken that the precipitate did not climb too high up the funnel's walls.* The precipitate was filtered out, and the resultant hydrochloric mother liquor was chilled to 0-2° and then again used to treat the precipitate on the funnel. This processing was repeated another 3 or 4 times, after which the resulting precipitate of 1-amino-2-naphthol hydrochloride was squeezed out well and washed twice with ether. The precipitate together with the funnel was dried to constant weight at 30-40° in vacuum, first in a current of air that had first been passed through two Tishchenko bottles filled with an alkaline solution of pyrogallol, and then – after the odor of hydrochloric acid had disappeared – without any air.

We usually got 0.98 g of ash-free 1-amino-2-naphthol hydrochloride, i.e., 98% of the original substance.

Found %: N 7.26; $C_{10}H_{10}ONCl$. Computed %: N 7.16.

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* To prevent this it is sometimes advisable to apply a slight vacuum.

2. Behavior of 1-amino-2-naphthol with an aqueous solution of sulfuric acid. a) 1.00 g of freshly crystallized 1-amino-2-naphthol was dissolved at 20° in 50 ml of a 1% solution of sulfuric acid containing 0.1% sulfurous acid. The resulting solution was allowed to stand in a closed flask for 4 hours at 20°. Then a solution of 5.3 g of sodium acetate trihydrate, saturated in the cold, was added to it. 1-Amino-2-naphthol was thrown down at once as a white precipitate, its weight being determined by the method described above. This yielded 0.98 g of 1-amino-2-naphthol hydrochloride, or 98% of the initial substance.

Found %: N 7.19. $C_{10}H_{10}ONCl$. Computed %: N 7.16.

b) A similar test was run with a 5% solution of sulfuric acid, the only change being that 18.5 g of sodium acetate was used to precipitate the 1-amino-2-naphthol base. This yielded 0.98 g of 1-amino-2-naphthol hydrochloride, or 98% of the initial quantity. In both instances, therefore, the 1-amino-2-naphthol hydrochloride was recovered in a quantitative yield, whence it follows that it cannot be sulfonated to 1-amino-2-naphthol-4-sulfonic acid under these conditions.

3. Behavior of 1-amino-2-naphthol with an aqueous solution of sulfurous acid in the presence of atmospheric oxygen. A solution of 1.00 g of freshly recrystallized 1-amino-2-naphthol hydrochloride in 50 ml of 5.3% sulfurous acid was placed in a flask fitted with a reflux condenser and connected to a gasometer. 0.69 g of sodium acetate trihydrate was added to the resulting yellowish solution to neutralize the hydrogen chloride contained in the 1-amino-2-naphthol hydrochloride. Then a current of air was passed through the reaction solution for 4 hours at 20° at a rate of about 2 liters per hour.* Then an aqueous solution of sodium acetate saturated in the cold was added. The white precipitate of the 1-amino-2-naphthol base was converted into the hydrochloride as described in Experiment 1. This yielded 0.97 g of 1-amino-2-naphthol hydrochloride, or 97% of the initial quantity.

Inasmuch as the initial 1-amino-2-naphthol hydrochloride was recovered in a practically quantitative yield in this experiment, it is evident that it cannot be sulfonated to 1-amino-2-naphthol-4-sulfonic acid under these conditions.

SUMMARY

The status of the problem of the structure of the bisulfite derivatives of various types of aromatic compounds has been examined critically, namely: naphtholsulfo acids, naphthol- and aminoazo dyes, nitroso- and aminonaphthols, resorcinol, and benzeneazobenzenehydrazonaphthalenes.

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* It was found in a preliminary test that by the end of the run the initial 5.3% solution of sulfurous acid contained 0.87% sulfurous acid, after air had been blown through the solution for 4 hours under the conditions specified above.

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* See C.B.Translation, pp. 2185.

SULFONATION AND SULFO ACIDS OF ACIDOPHOBIC COMPOUNDS

XVI. THE SULFONATION OF SOME DERIVATIVES OF INDOLE

A. P. Terentyev and L. A. Yanovskaya

Continuing our research on the sulfonation of pyridine sulfotrioxides of the indoles [1], we have sulfonated some derivatives of indole, namely: 2-phenylindole, 3-indolylacetic acid, 3-acetylindole, and 1-acetylindole. 2-Phenylindole was sulfonated with pyridine sulfotrioxide at 120-130°, producing a beautiful yield (95%) of 2-phenylindolesulfonic acid, which we isolated as the barium salt, which is rather sparingly soluble in water; the salt crystallizes as leaflets. Bromine water is decolorized by a salt solution in the cold, though the sulfo group is not split off, as it is in indolesulfonic-2 and 3-methylindolesulfonic-2 acids. Hydrolysis with 15% hydrochloric acid takes 6-8 hours, the sulfo group being split off as sulfurous acid.

Hence, its chemical properties indicate that this acid must contain the sulfo group at the β-position in the heterocyclic portion of the indole molecule, i.e., its structure is that of 2-phenylindolesulfonic-3 acid. This structure was confirmed by oxidation with an alkaline permanganate solution, yielding benzoylanthranilic acid. 3-Indolylacetic acid is readily sulfonated by pyridine sulfotrioxide at 100-110°, producing a 98% yield of 2-sulfo-3-indolylacetic acid, isolated as its barium salt, which is freely soluble in water. A solution of the salt decolorizes bromine water, the sulfo group being split off as barium sulfate. A 15% solution of hydrochloric acid hydrolyzes it rapidly, within 5-10 minutes, sulfur dioxide being evolved. 3-Acetylindole is sulfonated at 140°. The reaction is incomplete, the yield of 3-acetylindolesulfonic acid, as its barium salt, not exceeding 55%. A solution of the salt decolorizes bromine water in the cold, yielding barium sulfate. 1-Acetylindole is sulfonated with difficulty, only at 130-140°, 1-acetylindolesulfonic acid being produced with a yield of some 50%. The structure of the acid is borne out by the fact that solutions of its barium salt decolorize bromine water in the cold, the sulfo group being split off as barium sulfate. We also tested the action of pyridine sulfotrioxide on 3-dimethylaminomethylindole and 3-diethylaminomethylindole at 100°. The sulfo mass darkened considerably in both cases; we recovered small quantities of the barium salts of the sulfo acids, but were unable to secure these salts in an analytically pure state.

EXPERIMENTAL

Sulfonation of 2-phenylindole. The 2-phenylindole was prepared by the E. Fischer method [2]. M.p. of the preparation 185°. 1.93 g of 2-phenylindole was sulfonated in a sealed ampoule for 8 hours with 4.77 g of pyridine sulfotrioxide dissolved in 5 ml of dichlcroethane, at 120-130°. The resultant light-brown

sulfo mass was washed with a small quantity of ether to remove the unreacted indole and then boiled with an aqueous suspension of barium carbonate until all the pyridine had been eliminated. The residue was extracted with boiling water several times and then filtered out and evaporated until crystallization set in. This yielded 3.25 g of the barium salt, representing a 95% yield, based on the monosulfo acid.

4.769 mg substance: 1.627 mg $BeSO_4$. 4.671 mg substance: 1.588 mg $BaSO_4$. Found %: Ba 20.08, 20.01: $(C_{14}H_{10}O_3NS)_2Ba$. Computed %: Ba 20.15.

The sodium salt was secured from the barium salt by adding sodium sulfate. It is freely soluble in water.

Oxidation of the sodium salt with permanganate. 1.5 g of the sodium salt was oxidized in the cold with an excess of a 2% solution of potassium permanganate. The mixture was allowed to stand overnight. The excess permanganate was eliminated with a few drops of alcohol. After the manganese dioxide had been filtered out, the sulfate ion was detected in the filtrate, i.e., the sulfo group had been split off during oxidation. When the filtrate was carefully acidulated, a crystalline precipitate (1 g) was thrown down. It had a m.p. of 179-180° after refining by reprecipitation from a dilute alkali, which is close to the figure given in the literature for benzoylanthranilic acid (m.p. 181°) [3].

Sulfonation of 3-indolylacetic acid. The preparation at our disposal had a m.p. of 164°, which conforms to the figure given in the literature [4]. 1 g of 3-indolylacetic acid was sulfonated for 10 hours at 100-110° with 2.8 g of pyridine sulfotrioxide dissolved in dichloroethane. The barium salt of 2-sulfo-3-indolylacetic acid was recovered after suitable processing with an aqueous suspension of barium carbonate, involving boiling, extraction, evaporation, and precipitation with methanol. This yielded 2.2 g of the salt (98% yield).

4.891 mg substance: 2.909 mg $BaSO_4$. 4.221 mg substance: 2.533 mg $BaSO_4$. Found %: Ba 35.00, 35.39: $C_{10}H_7O_5NSBa$. Computed %: Ba 35.12.

Sulfonation of 3-acetylindole. The 3-acetylindole was prepared by the Zatti and Ferratini method [5]. M.p. of the preparation 190° (from benzene), which agrees with the figure given in the literature. 1.59 g of 3-acetylindole was sulfonated for 12 hours at 140° with 4.77 g of pyridine sulfotrioxide dissolved in dichloroethane. The usual processing yielded 1.68 g of the barium salt of 3-acetylindolesulfonic-2 acid (55% yield), which was freely soluble in water.

8.401 mg substance. 3.212 mg $BaSO_4$. 8.049 mg substance: 3.083 mg $BaSO_4$. Found %: Ba 22.50, 22.54. $(C_{10}H_8O_4NS)_2Ba$. Computed %: Ba 22.46.

Sulfonation of 1-acetylindole. The 1-acetylindole was prepared from indolemagnesium bromide and ethyl acetate by our own process. The boiling point of the preparation was 148-150° (at 10 mm); n_D^{20} 1.6100; d_4^{20} 1.387; MR_D 39.50; computed 39.43. Literature data: b.p. 152-153° (at 14 mm) [5].

1.59 g of 1-acetylindole was sulfonated at 130-140° with 4.77 g of pyridine sulfotrioxide dissolved in dichloroethane. The usual treatment yielded 1.65 g of the barium salt of the monosulfo acid (50% yield).

9.111 mg substance: 3.501 mg $BaSO_4$; 6.908 mg substance: 2.665 mg $BaSO_4$. Found %: Ba 22.61, 22.70. $(C_{10}H_8O_4NS)_2Ba$. Computed %: Ba 22.46.

SUMMARY

1. Pyridine sulfotrioxide is a suitable sulfonating agent for indole derivatives.

2. The 2-phenylindolesulfonic-3, 2-sulfo-3-indolylacetic, 3-acetylindolesulfonic-2, and 1-acetylindolesulfonic-2 acids have been synthesized for the first time and isolated as their barium salts.

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* See C.B. Translation p. 763.

THE NITRATION OF DIPHENYLUREA (CARBANILIDE)

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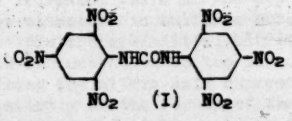
Losanitch [1] was the first to make a more or less authentic report on the nitration of carbanilide. Reacting carbanilide with cold concentrated nitric acid, he invariably produced tetranitrodiphenylurea; he found its melting point to lie above 200°. At nearly the same time Fleischer [2] reacted concentrated nitric acid with carbanilide and secured a yellow product that was insoluble in alcohol. Reducing the latter, he obtained diaminocarbanilide as the reduction product. This indicated that the nitration product was a dinitro product, though the structure of this dinitro product was not established. Reudler, who made a rather thorough study of the nitration of carbanilide, believed [3] that Fleischer's analytical results were undependable and that the reduction product he said he had secured was unlikely, since the reduction should have yielded a tetramino derivative of carbanilide. Perkin [4] treated Losanitch's tetranitrocarbanilide with equal parts of nitric and sulfuric acids and secured a new substance with a m.p. of 203°, which yielded 1,4,6-trinitroaniline when heated with ammonia; hence, the nitration product was considered to be 2,4,6,2',4',6'-hexanitrocarbanilide (I). This last bit of evidence likewise makes it appear that the product synthesized by Losanich was 2,4,2',4'-tetranitrocarbanilide (II).

Curtius [5] arrived at quite different and unexpected results. Reacting nitric acid with carbanilide without the use of any heat, he secured a yellow precipitate that yielded m-nitroaniline when hydrolyzed. This led Curtius to conclude that the nitration product was 3,3'-dinitrocarbanilide (III). Reudler [3] nitrated carbanilide repeatedly under the conditions used by Curtius and then varied the conditions, but was never able to secure 3,3'-dinitrocarbanilide, the nitration product invariably being 2,4,2',4'-tetranitrocarbanilide. Lastly, Tingle and Blanck [6] were of the opinion that during nitration the sulfuric acid might form an unstable compound that prevented substitution at the ortho and para positions and oriented the nitro group to the meta position. This was not confirmed, however; moreover, we cannot fail to note that Curtius' nitration took place without any sulfuric acid present.



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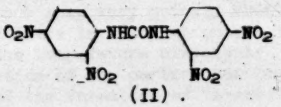

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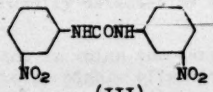


(III)

The foregoing appears to show that: 1) there is no agreement regarding the position of the nitro groups entering carbanilide or their number; 2) no one has ever described the direct synthesis of 4,4'-dinitrocarbanilide, a compound that is of interest in many respects, via the nitration of carbanilide. Moreover, whenever it has been necessary to have 4,4'-dinitrocarbanilide (IV), it has been prepared by treating p-nitroaniline with phosgene [7]:

(IV)

The orienting group during nitration of carbanilide is the carbamide group $-NH\cdot CO\cdot R-$, as in numerous other instances of the nitration of acylated derivatives of aniline. And as the nitro group enters chiefly at the para position to the acylated amino group, and only occasionally in the ortho position, in all these numerous instances of nitration (of formanilide, acetanilide, oxanilide, etc.), we thought we would also secure mainly the 4,4'-dinitrocarbanilide by nitrating carbanilide. Only when more severe nitration conditions were used (high concentration of nitric acid, high temperature, and the like) could we expect to get more highly nitrated products. We were therefore interested in studying the nitration of carbanilide and in finding the conditions under which the principal product would be a 4,4'-dinitro substitution derivate.

For nitration purposes the carbanilide was dissolved in sulfuric monohydrate, and 68% nitric acid was added to the solution at 0-1°, the nitration product settling out as a yellow precipitate, and the reaction mass being poured over ice. After the precipitate had been dried, it had a m.p. of 296-299°, melting at 310.5° after recrystallization from pyridine, this latter being the m.p. of p,p'-dinitrocarbanilide. This structure is also borne out by the ultimate analysis of the product. For further proof of the structure of the p,p'-dinitroanilide, it was hydrolyzed with sulfuric acid, yielding p-nitroaniline with a m.p. of 147°. Under these conditions no traces of tetranitrocarbanilide could be found, since the solution was not colored red by the addition of a concentrated solution of sodium hydroxide.

Raising the nitration temperature from 0° to 50° raised the yield of the crude dinitro product of the nitration of carbanilide in the monohydrate solution only up to a certain limit, 15°, above which the yield of p,p'-dinitrocarbanilide begins to drop off. The melting point of the crude p,p'-dinitrocarbanilide rose almost parallel with the increase in yield. In addition to the temperature, another factor affecting the yield of the p,p'-dinitrocarbanilide is the concentration of the nitric acid added to the monohydrate solution of the carbanilide, the yield of the crude p,p'-dinitrocarbanilide rising only up to a certain nitric acid concentration (48-67%), after which it drops off. As before, the melting point of the crude product rises more or less parallel with the increased yield of the p,p' dinitrocarbanilide. Our experiments have shown that nitration in sulfuric monohydrate solution does not afford a high yield of 4,4'-dinitrocarbanilide; nitration comes to a stop very quickly when the nitric acid concentration is too low or the temperature is not high enough, while raising the nitric acid concentration or the temperature diminishes the yield, apparently as the result of the disintegration of the carbanilide or of its nitro substitution derivate, and as the result of the formation of tetranitrocarbanilide, the latter being readily detected by the formation of a red solution when a strong base is added.

The nitration method in which the carbanilide was not dissolved, but was in suspension, proved to be highly effective. This nitration method is employed, for example, in the synthesis of p-nitro-o-anisidine, the nitration being effected

at 80-85° with 10% nitric acid [8]. Nitrating carbanilide in aqueous suspension at 80° with 20% nitric acid increased the yield immediately: 5 g of the carbanilide yielded 5.81 g of the dinitrocarbanilide, which had a m.p. of 310° after being recrystallized. The yield was 69% based on the nitrite. The best nitrating temperature was found to be 90° (Fig. 1).

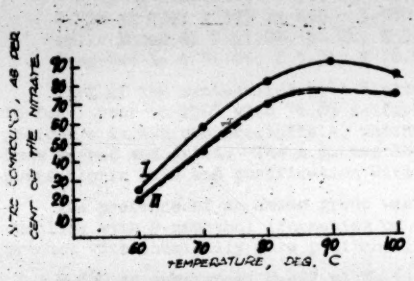


Fig. 1. Effect of temperature on the nitration of carbanilide in aqueous suspensions by nitric acid.
I - Nitration with 30% nitric acid; II - nitration with 20% nitric acid.

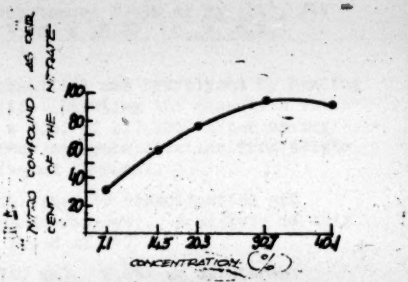
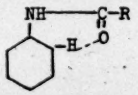


Fig. 2. Effect of the nitric acid concentration upon the nitration of carbanilide in aqueous suspension.

In none of our experiments were we able to detect the formation of m,m'-dinitrocarbanilide. This is in complete harmony with the well-known fact that all the derivatives of aniline that are acylated by carboxylic acids and hence contain the -NH·CO·R- group are nitrated mainly at the para position, only occasionally being nitrated at the ortho position. We thought it would be of interest to determine the effect of the concentration of nitric acid upon nitration in aqueous suspension. To do this we effected nitration at the same temperature of 90° with nitric acid whose concentration ranged from 7.1 to 40.1%. The results of these tests are shown in Fig. 2.

As we see, the 30% nitric acid is the most effective; any lower concentration greatly diminishes the yield of the nitro product, while raising the concentration above 30% does not increase the yield perceptibly.

In distilling the hydrolysis products with steam we observed the deposition of a yellow product upon the condenser tube, the m.p. of this product being close to that of o-nitroaniline. This negligible formation of the ortho isomer during nitration might be due to the formation of an internal hydrogen bond between the oxygen of the carbonyl group and the hydrogen atom in the ortho position to the nitrogen.



EXPERIMENTAL

1. Nitration of carbanilide in a sulfuric acid solution. 5 g (0.024 mole) of carbanilide, with a m.p. of 239°, was dissolved in 15 g of sulfuric monohydrate, the solution being chilled externally by ice. The solution was continuously stirred as 5 g (0.054 mole) of 68.28% nitric acid was added a drop at a time, the temperature being maintained at 0°. After all the acid had been added, stirring was continued for another 2 hours at 0°,

and then the mass was poured out into a mixture of ice and water. The finely crystalline, bright-yellow precipitate was filtered out, washed with water, and dried at 70-90°, yielding 2.4 g of the dry product, with a m.p. of 296-299°. The solution was not turned red when sodium hydroxide solution was added (no tetranitrocarbanilide present). M.p. 310.5° after recrystallization from pyridine.

3.4962 mg substance: 6.542 mg CO_2; 1.130 mg H_2O. 4.0178 mg substance: 7.552 mg CO_2; 1.330 mg H_2O. 3.080 mg substance: 0.498 ml N_2 (21°, 744 mm). Found %: C 51.02, 51.26; H 3.62, 3.70; N 18.22. $C_{13}H_{10}O_5N_4$. Computed %: C 51.65; H 3.31; N 18.54.

Part of the synthesized 4,4'-dinitrocarbanilide was hydrolyzed by heating it for 1 hour to 150° with 74.8% sulfuric acid. Diluting the mass with water yielded a dark-brown precipitate, which had a m.p. of 127-128° after having been washed and dried. The m.p. was 147° after recrystallization from dilute hydrochloric acid and purification with activated charcoal.

The presence of an amino group was established by diazotization and coupling with β-naphthol (formation of an orange-red dye). A mixture of this product with chemically pure p-nitroaniline fused at 147°.

2.380 mg substance: 0.422 ml N_2 (18°, 747 mm). 2.494 mg substance: 0.440 ml N_2 (21°, 762 mm). Found %: N 20.12, 20.14. $C_6H_6O_2N_2$. Computed %: N 20.29.

2. Effect of the concentration of nitric acid upon the nitration of carbanilide in sulfuric acid. In the ensuing experiments, 5 g of carbanilide was dissolved in 20 g of sulfuric monohydrate; nitration was effected by nitric acid of various concentrations, the total amount of 100% HNO_3 in each test being 2.9 g. The nitration temperature was 15°, and it lasted 1 hour 30 minutes. Recovery of the product was the same as indicated above. The results are shown in Table 1.

TABLE 1

Test No.	Concentration of nitric acid, %	Yield of pure dinitrocarbanilide, g	M.p. of crude dinitrocarbanilide
1	8.40	4.30	245
2	18.40	4.62	280
3	24.79	4.95	275
4	30.00	5.05	304
5	37.70	5.20	295
6	48.59	5.10	290
7	57.23	5.10	2.78
8	67.46	5.0	270
9	73.30	4.52	255
10	84.60	4.1	246

TABLE 2

Test No.	Nitration temperature	Grams of crude nitro product	M.p. of crude nitro product
1	0°	5.02	275-276°
2	10	5.04	288-295
3	15	5.40	300-301
4	20	5.32	295-298
5	30	5.25	276-280
6	40	5.05	270-275
7	40	5.0	260-265

3. Effect of temperature on the nitration of carbanilide in sulfuric acid. In the following experiments 5 g of carbanilide was dissolved in 20 g of sulfuric monohydrate; nitration was effected with 9.7 g of 30% nitric acid at various temperatures, ranging from 0 to 50°. Nitration lasted 1.5 hours. The recovery and refining of the product were the same as in the preceding tests. The results are given in Table 2.

4. Nitration of carbanilide in an aqueous suspension by dilute nitric acid. 40 g of 20% nitric acid was placed in a round-bottomed flask fitted with a stirrer and a reflux condenser, and then 5 g of pure carbanilide, with a m.p. of 239°, was added at room temperature, with constant stirring. The mass was then heated to 80° for 3 hours and kept at that temperature for another 5 hours. The white crystals of carbanilide turned yellow rather quickly. The reaction mass was chilled, and the yellow precipitate was filtered out, washed with cold water, and dried. This yielded 5.81 g of the dry product, with a m.p. of 254°. The resultant nitro product was hydrolyzed by heating it in an autoclave with 150 ml of a 4.5% solution of ammonia for 5 hours to 150°, yielding 3.4 g of a dark-green dry product with a m.p. of 128-130°. The latter was distilled with steam to eliminate the aniline and any possible isomers of p-nitroaniline. When the distillate was alkalinized, a yellow-orange crystalline precipitate was thrown down, weighing 0.2 g after drying, with a m.p. of 62°; recrystallization from water yielded a bright-yellow product with a m.p. of 69-70° (the melting point of chemically pure orthonitroaniline is 72°). The residue left in the flask after the steam distillation yielded 1.8 g of dry paranitroaniline, with a m.p. of 147°, after drying.

TABLE 3

Test No.	Nitration temperature	Grams of nitro product	M.p. of the nitro product	Nitro product as per cent of carbanilide (determined against nitrite)
1	60°	5.1	252°	24.5
2	70	5.35	259	59.5
3	80	5.8	278	82.5
4	90	6.49	300	93.4
5	100	5.89	281	86.9

5. Effect of temperature upon the nitration of carbanilide in aqueous suspension with 20% nitric acid. Nitration lasted 7 hours. The nitration temperature varied from 60 to 100°, 5 g of carbanilide being nitrated in each run. The results are listed in Table 3.

6. Effect of temperature upon the nitration of carbanilide in aqueous suspension, with 30% nitric acid. Nitration lasted 7 hours, 5 g of carbanilide being nitrated in each run. The results are listed in Table 4.

TABLE 4

Test No.	Nitration temperature	Grams of nitro product	M.p. of the nitro product	Nitro product as % of carbanilide (determined against nitrite)
1	60°	5.04	242°	20.5
2	70	5.12	253	40.6
3	80	5.34	269	70.6
4	90	5.6	276	77.6
5	100	5.5	274	76.1

7. Effect of nitric acid concentration upon the nitration of carbanilide in aqueous suspension. 5 g of carbanilide was mixed with 40 g of nitric acid, the concentration of which was varied from 7 to 40%. The mixture was gradually heated to 90° and then stirred for 5 hours at that temperature. After the mixture had cooled, the nitro product was filtered out, the percentage of the latter being determined by reduction and titration with a nitrite solution. The results are given in Table 5.

8. Combined effect of temperature and length of reaction upon the nitration of carbanilide in aqueous suspension with 30% nitric acid. 200 g of 30% nitric acid and 20 g of finely powdered carbanilide were placed in a 500-ml flask

and the mixture was heated to 60° and kept at that temperature for one hour. Then its temperature was raised to 70°, and kept there for another hour, the temperature of the mass being raised step-by-step to 100° in this manner. A sample was taken for analysis at the end of each constant-temperature period, the precipitate being filtered out of each sample, washed, and dried. After reduction, the quantity of nitro product synthesized was determined by nitration against a sodium nitrite solution (determination against nitrite). The results are listed in Table 6.

TABLE 5

Test No.	Concentration nitric acid, %	Grams of nitro product	M.p. of the nitro product	Nitro product as % of carbanilide (determined against nitrite)
1	7.1	5.07	245°	30.2
2	14.5	5.52	252	58.5
3	20.3	5.95	274	76.1
4	30.7	6.51	299	93.8
5	40.1	6.50	296	92.0

TABLE 6

Test No.	Reaction temperature, (°)	% of nitro compound in sample	M.p. of the nitro product
1	60°	19.5	241°
2	70	48.6	247
3	80	80.77	278
4	85	87.96	282
5	90	92.37	294.5
6	95	91.24	294
7	100	90.07	-

SUMMARY

1. Orientation in the nitration of carbanilide is no different from the orientation in the nitration of other acylated derivatives of aniline.

2. Nitration of carbanilide in sulfuric monohydrate or in aqueous suspension yields different quantities of 4,4'-dinitrocarbanilide.

3. There are practical advantages in securing 4,4'-dinitrocarbanilide by nitrating carbanilide in aqueous suspension at 90° with 30% nitric acid.

4. Curtius' idea that m,m'-dinitrocarbanilide is formed when carbanilide is nitrated is wrong.

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RESEARCHES ON ORGANIC POLYSULFIDES. III.

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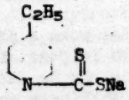
Pursuing our synthesis researches on thiuram polysulfides, we were interested in using γ-ethyl- and γ-isopropylpiperidines as the initial bases, since they contained different substituents at the same position in the ring. Our previous research had shown [1] that γ-methylpiperidine yields a stable thiuram tetrasulfide.

We also assumed that stereoisomerism would have to be manifested somehow in the properties of polysulfide accelerators. We used trans- and cis-decahydroquinolines in our syntheses of thiuram polysulfides in order to determine the effect of isomerism.

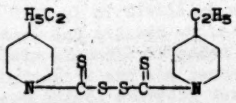
γ-Ethylpiperidine [2] condenses vigorously with carbon disulfide. When sodium hydroxide is present, it condenses to yield the sodium salt of γ-ethyl piperidyldithiocarbamic acid (I). If an excess of the original base is used in the reaction instead of the sodium hydroxide, we get the γ-ethylpiperidyldithiocarbamate of γ-ethylpiperidine. We have also synthesized the zinc salt of γ-ethylpiperidyldithiocarbamic acid. Reacting γ-ethylpiperidyldithiocarbamates with sulfur monochloride yields a tacky, resinous compound that cannot be refined.

We tried to react the γ-ethylpiperidyldithiocarbamates with sulfur monochloride under various conditions changing the reaction temperature, using different dithiocarbamates, but the reaction always yielded a resinous substance.

Oxidizing the sodium salt of γ-ethylpiperidyldithiocarbamic acid with iodine in absolute alcohol yielded γ-ethylpiperidylthiuram disulfide (II).

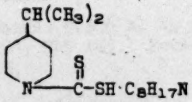


(I)



(II)

Like ethylpiperidine, γ-isopropylpiperidine [3] condenses readily with carbon disulfide, yielding the γ-isopropylpiperidine salt of γ-isopropylpiperidylcarbamic acid (III). Condensation with carbon disulfide and sodium hydroxide yields the sodium salt of γ-isopropylpiperidyldithiocarbamic acid (IV).



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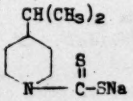
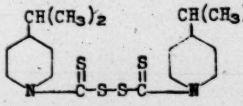


(IV)

We also prepared the zinc and nickel salts. The thiuram disulfide (V) was synthesized by oxidizing the sodium dithiocarbamate with iodine in alcohol.



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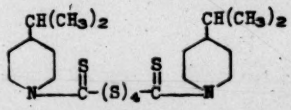
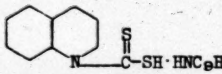


(VI)

Reacting sodium γ-isopropylpiperidyldithiocarbamate with sulfur monochloride yielded the thiuram tetrasulfide (VI), a compound that is stable when stored.

The trans- and cis-decahydroquinolines [4] condense readily with carbon disulfide, yielding the decahydroquinolyldithiocarbamate of decahydroquinoline (VII). With sodium hydroxide we secured the sodium salts of the trans- and cis-decahydroquinolyldithiocarbamic acids (VIII).



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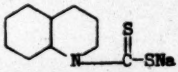
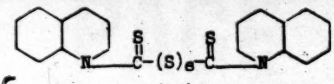


(VIII)

The latter were converted into their zinc salts by reacting them with zinc acetate.

Treating the zinc dithiocarbamates of trans- and cis-decahydroquinoline with sulfur monochloride yields thiuram hexasulfides (IX), which are stable under storage.



(IX)

EXPERIMENTAL

The sodium salt of γ-ethylpiperidyldithiocarbamic acid. A solution of 0.3 g of γ-ethylpiperidine in 15 ml of absolute alcohol was mixed with a solution of 0.11 g of sodium hydroxide in 0.25 ml of distilled water. Then the mixture was chilled with a snow-salt mixture and stirred while a solution of 0.21 g of carbon disulfide in 5 ml of absolute alcohol was added a drop at a time. (Theoretical quantities of the sodium hydroxide and the carbon disulfide were used.) After the carbon disulfide had been added, stirring was continued, without chilling, for one hour. Most of the alcohol was driven out of the resulting alcoholic solution of the sodium salt in vacuum (without the use of heat), white crystals with a m.p. of 203° settling out of a concentrated ether solution. The yield was 0.55 g (almost quantitative). The sodium salt is soluble in methanol, ethyl alcohol, water, and acetone at room temperature; it is insoluble in benzene, ether, etc. The m.p. of the ether-precipitated salt was 205° after recrystallization from an alcoholic solution.

5.180 mg substance: 0.306 ml N_2 (20°, 745 mm). 6.190 mg substance: 0.354 ml N_2 (20°, 745 mm). Found %: N 6.74, 6.53. $C_8H_{14}NS_2Na$. Computed %: N 6.63.

The zinc salt of γ-ethylpiperidyldithiocarbamic acid is sparingly soluble

in hot benzene and hot chloroform, but is insoluble in the other customary solvents. It crystallizes from benzene as minute white crystals with a m.p. of 198-200°.

2.650 mg substance: 0.150 ml N_2 (20°, 741 mm). Found %: N 6.43. $C_{16}H_{28}N_2S_4Zn$. Computed %: N 6.34.

γ-Ethylpiperidine salt of γ-ethylpiperidyldithiocarbamic acid. A chilled solution of 0.15 g of carbon disulfide in 3 ml of absolute ether was added to an ice-water-chilled solution of 0.5 g of γ-ethylpiperidine in 6 ml of absolute ether (molar proportions of the reagents 2:1). Shortly thereafter flocculent colorless crystals, with a m.p. of 139-140°, settled out of the solution. They were freely soluble in alcohol, but sparingly so in ether, ligroin, or water. The substance's m.p. was 141.5-142° after recrystallization from alcohol. The yield was 0.65 g (97% of the theoretical).

2.240 mg substance: 0.180 ml N_2 (23°, 745 mm). 4.762 mg substance: 0.382 ml N_2 (21°, 745 mm). Found %: N 9.08, 9.13. $C_{15}H_{30}N_2S_2$. Computed %: N 9.26.

Thiuram disulfide of γ-ethylpiperidine. 0.3 g of the sodium salt of γ-ethylpiperidyldithiocarbamic acid was dissolved in the minimum quantity of absolute alcohol. An alcoholic solution of iodine, saturated while hot, was added to the solution a little at a time until the former was no longer decolorized. As the iodine solution was added, the yellow precipitate of the disulfide was thrown down. The latter was washed with water, alcohol, and ether and purified by recrystallization from alcohol. M.p. 98-98.5°.

3.190 mg substance: 0.210 ml N_2 (19°, 743 mm). 3.595 mg substance: 0.233 ml N_2 (18°, 751 mm). Found %: N 7.52, 7.54. $C_{16}H_{28}N_2S_4$. Computed %: N 7.44.

γ-Isopropylpiperidine salt of γ-isopropylpiperidyldithiocarbamic acid. 0.4 g of the base was dissolved in 2 ml of absolute ether, chilled with ice, and then mixed with a chilled solution of 0.15 g of carbon disulfide in 1 ml of ether. White crystals, totaling 0.43 g (74% of the theoretical) were precipitated at once. The crystals were recrystallized from alcohol as lustrous flakes with a m.p. of 154.5-155°.

2.810 mg substance: 0.204 ml N_2 (22°, 748 mm). 3.445 mg substance: 0.245 ml N_2 (19°, 758 mm). Found %: N 8.53, 8.29. $C_{17}H_{34}N_2S_2$. Computed %: N 8.47.

Sodium salt of γ-isopropylpiperidyldithiocarbamic acid. A solution of 0.16 g of sodium hydroxide in 0.25 ml of water was added to a solution of 0.5 g of the base in 10 ml of absolute alcohol. Then a solution of 0.33 g of carbon disulfide in 2 ml of absolute alcohol (a 10% excess of carbon disulfide) was added drop by drop while the solution was stirred and chilled with an ice-salt mixture, after which the reaction mass was stirred for an hour without chilling. The resultant alcoholic solution was concentrated in vacuum; when ether was added to it, 0.82 g (92.1% of the theoretical) of the white crystals of the sodium salt settled out. It crystallized as snow-white crystals with a m.p. of 197-198° as the result of adding ether to the alcoholic solution until the latter grew slightly cloudy.

2.570 mg substance: 0.139 ml N_2 (21°, 748 mm). 2.286 mg substance: 0.120 ml N_2 (19°, 758 mm). Found %: N 6.18, 6.12. $C_9H_{16}NS_2Na$. Computed %: N 6.22.

Zinc salt of γ-isopropylpiperidyldithiocarbamic acid. M.p. 188-189°.

The m.p. was 189° after recrystallization from a benzene-ether mixture.

3.670 mg substance: 0.195 ml N_2 (24°, 748 mm). 2.922 mg substance: 0.151 ml N_2 (21°, 748 mm). Found %: N 6.01, 5.91. $C_{18}H_{32}S_4Zn$. Computed %: N 5.96.

Thiuram disulfide of γ-isopropylpiperidine. This was prepared by oxidizing the sodium salt with iodine in alcoholic solution. After recrystallization from ether the disulfide had a m.p. of 127°.

2.672 mg substance: 0.165 ml N_2 (21°, 746 mm). 1.566 mg substance: 0.098 ml N_2 (22°, 746 mm). Found %: N 7.05, 7.11. $C_{18}H_{32}N_2S_4$. Computed %: N 6.92.

Thiuram tetrasulfide of γ-isopropylpiperidine. A solution of 0.18 g of sulfur monochloride in 5 ml of absolute ether (a 20% excess of S_2Cl_2) was added to 0.5 g of the sodium salt of γ-isopropylpiperidyldithiocarbamic acid dissolved in 8 ml of absolute ether. The reaction mixture was chilled with ice, and stirring was continued for two hours without any chilling. Driving off part of the ether in vacuum caused 0.3 g (57.7% of the theoretical) of yellowish crystals with a m.p. of 91-92° to settle out of the solution. They crystallized from ether as lustrous flakes with a m.p. of 93°.

0.1202 g substance: 0.3588 g $BaSO_4$. 2.327 mg substance: 0.115 ml N_2 (21°, 757 mm). 3.035 mg substance: 0.148 ml N_2 (22°, 755 mm). Found %: S 40.98; N 5.71, 5.61. $C_{18}H_{32}N_2S_4$. Computed %: S 41.05; N 5.98.

Sodium salt of trans-decahydroquinolyldithiocarbamic acid. A solution of 0.5 g of trans-decahydroquinoline in 15 ml of ether was added to a solution of 0.17 g of sodium hydroxide in 0.35 ml of water. Then the solution was well stirred and chilled with a snow-and-salt mixture while a solution of 0.33 g of carbon disulfide in 5 ml of ether (a 20% excess of sodium hydroxide and carbon disulfide) was added a drop at a time. After the carbon disulfide had been added, stirring was continued for one hour without chilling. The precipitated minute crystals of the sodium salt were suction-filtered out, washed with ether, and desiccated with phosphorus anhydride. The yield was 0.83 g (95.3% of the theoretical).

The sodium salt had a m.p. of 118° after recrystallization by the addition of ether to an alcoholic solution until the latter turned cloudy.

The sodium salt of trans-decahydroquinolyldithiocarbamic acid was likewise synthesized in alcohol.

A solution of 0.14 g of sodium hydroxide in 0.3 ml of water was mixed with a solution of 0.5 g of trans-decahydroquinoline in 10 ml of alcohol. The liquid was stirred and chilled with a snow-and-salt mixture while a solution of 0.28 g of carbon disulfide in 2 ml of alcohol was added. (The theoretical quantities of sodium hydroxide and carbon disulfide were used.) Most of the alcohol was driven off from the resultant slightly yellowish solution at room temperature in vacuum, the white crystals of the sodium salt being precipitated from the residue by ether. The sodium salt, recrystallized from an alcoholic solution by adding ether until the solution turned cloudy (with no heat applied), had a m.p. of 118°. The yield was 0.5 g (58.2% of the theoretical).

The m.p. of the zinc salt of trans-decahydroquinolyldithiocarbamic acid was 122-123°. It was crystallized from a benzene-alcohol mixture as minute yellowish crystals with a m.p. of 123°.

3.236 mg substance: 0.158 ml N_2 (23°, 734 mm). 3.436 mg substance: 0.169 ml N_2 (23°, 734 mm). Found %: N 5.44, 5.47. $C_{20}H_{32}N_2S_4Zn$. Computed %: N 5.67.

Thiuram disulfide of trans-decahydroquinoline. 0.3 g of the sodium salt of trans-decahydroquinolyldithiocarbamic acid was oxidized with an alcoholic solution of iodine. The alcoholic solution was concentrated in vacuum. The resultant precipitate was washed with water and desiccated with phosphoric anhydride, the yield being 0.25 g (95% of the theoretical). M.p. 81°.

Thiuram hexasulfide of trans-decahydroquinoline. A solution of 0.17 g of sulfur monochloride in 3 ml of absolute ether was added to 0.4 g of the zinc salt dissolved in 15 ml of absolute ether, and the reaction mass was stirred for two hours. The precipitate was suction-filtered out, washed with ether and with water until the zinc chloride was eliminated, and desiccated with phosphoric anhydride. The yield was 0.4 g (85.1% of the theoretical). M.p. 62-63°.

3.047 mg substance: 0.135 ml N_2 (23°, 742 mm). 2.980 mg substance: 0.131 ml N_2 (23°, 742 mm). 3.210 mg substance: 5.054 mg CO_2; 1.660 mg H_2O. 3.306 mg substance: 5.236 mg CO_2; 1.730 mg H_2O. 0.1203 mg substance: 0.4021 g $BaSO_4$. Found %: N 4.99; C 42.94; 43.19; H 5.79, 5.85; S 45.91. $C_{20}H_{32}N_2S_8$. Computed %: N 5.03; C 43.16; H 5.75; S 46.07.

The thiuram hexasulfide of trans-decahydroquinoline is freely soluble in benzene, chloroform, and carbon disulfide at room temperature, and is insoluble in ether, alcohol, or ligroin. Alcohol throws down a non-crystallizing yellow oil from benzene and carbon-disulfide solutions of the hexasulfide. When the solutions are evaporated in vacuum without the use of heat, a tacky oily product is left behind.

Derivatives of cis-decahydroquinolyldithiocarbamic acid were prepared under the same conditions as the trans-dithiocarbamates. The sodium salt of cis-decahydroquinolyldithiocarbamic acid, recrystallized by adding ether to its alcoholic solution until the latter turned cloudy, had a m.p. of 144° (the apparatus was preheated to 140°).

The zinc salt consisted of minute yellowish crystals (from a benzene-alcohol mixture) with a m.p. of 212°.

1.768 mg substance: 0.088 ml N_2 (24°, 749 mm). 2.888 mg substance: 0.142 ml N_2 (24°, 754 mm). Found %: N 5.64, 5.61. $C_{20}H_{32}N_2S_4Zn$. Computed %: N 5.67.

The cis-decahydroquinolyldithiocarbamate of cis-decahydroquinoline was crystallized from alcohol as colorless crystals with the m.p. of 137-138°.

2.948 mg substance: 0.208 ml N_2 (25°, 747 mm). 1.960 mg substance: 0.140 ml N_2 (23°, 747 mm). Found %: N 7.94, 8.09. $C_{19}H_{34}N_2S_2$. Computed %. N 7.90.

The thiuram disulfide of cis-decahydroquinoline has a m.p. of 129-130°; it is freely soluble in ether, benzene, and chloroform, and more sparingly in alcohol.

2.970 mg substance: 0.167 ml N_2 (23°, 749 mm). 2.969 mg substance: 0.165 ml N_2 (24°, 749 mm). Found %: N 6.39, 6.29. $C_{20}H_{32}N_2S_4$. Computed %: N 6.53.

The thiuram hexasulfide of cis-decahydroquinoline has a m.p. of 62-63°. It is as unstable in organic solvents as the thiuram hexasulfide of trans-decahydroquinoline.

0.1009 g substance: 0.3371 g $BaSO_4$. 2.871 mg substance: 0.125 ml N_2 (23°, 749 mm). 2.737 mg substance: 0.118 ml N_2 (26°, 752 mm). Found %: N 4.94, 4.93; S 45.79. $C_{20}H_{32}N_2S_8$. Computed %: N 5.03; S 46.07.

SUMMARY

1. A method has been developed for synthesizing the sodium, zinc, and γ-ethylpiperidine salts of γ-ethylpiperidyldithiocarbamic acid, and the thiuram disulfide of γ-ethyl piperidine has been synthesized.

2. A method has been developed for synthesizing the sodium, zinc, nickel, and γ-isopropylpiperidine salts of γ-isopropylpiperidyldithiocarbamic acid, and the thiuram disulfide and thiuram tetrasulfide of γ-isopropylpiperidine have been synthesized.

3. The decahydroquinoline, sodium, and zinc salts of the dithiocarbamic acids of trans- and cis-decahydroquinolines have been synthesized, as well as the thiuram disulfides and hexasulfides of the trans- and cis-decahydroquinolines.

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THE REACTIONS OF AZLACTONES (OXAZOLONES) WITH AMINES

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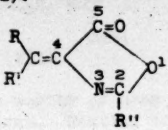
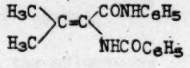
Not much work has been done on the reaction of azlactones of Type (I) with amines. The few papers on this topic indicate [1] that Type (I) azlactones react with primary and secondary amines to form amides of the respective acids. Research on this reaction has demonstrated, however, that the amides of these acids are secured when amines are condensed with those azlactones whose molecules contain hydrogen, an alkyl group, or an aryl group as the R and R' radicals. When we reacted 2-phenyl-4-isopropyliden-5-oxazolone and 2-phenyl(benzyl, methyl)-4-benzyliden-5-oxazolone with aniline, we secured the anilides of α-benzoylamino-β,β'-dimethylacrylic acid (II) and α-benzoyl(phenacyl, acetyl)-aminocinnamic acid (III).



(I)



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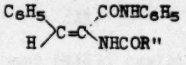
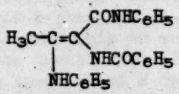


(III)

R'' = C_6H_5, $CH_2C_6H_5$, CH_3.

But when we began to investigate this reaction with azlactones in whose molecule the radical in the 4 position has a hydroxy or ethoxy group, we secured – in addition to the amides of the respective acids – amides of acids in which the hydroxy group had been replaced by the amino radical plus Type (I) azlactones containing an amino group instead of the hydroxy (or ethoxy) group.*

We used aniline and piperidine in our investigation of this reaction. In only one case – with 2-phenyl-4-(1-hydroxyethyliden)-5-oxazolone – did aniline react with the azlactone ring and with the hydroxy group, yielding the anilide of α-benzoylamino-β-phenylaminocrotonic acid (IV). In all the other cases, the amine reacted either with the azlactone ring or only with the hydroxy (or ethoxy) group; it should be said that only piperidine reacted with the azlactone ring, without affecting the hydroxy (or ethoxy) group at all, so that we secured piperidides of the respective acids. 2-Phenyl-4-(1-hydroxyethyliden)-5-oxazolone and piperidine, for example, yielded the piperidide of α-benzoylamino-β-hydroxycrotonic acid (V), whereas 2-phenyl-4-ethoxymethylen-5-oxazolone yielded the piperidide of α-benzoylamino-β-ethoxyacrylic acid (VI).



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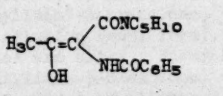

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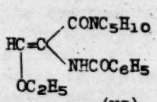
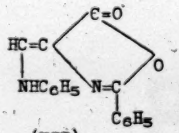


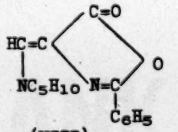
(VI)

* The formation of these compounds is evidence of the ability of the amine to react with the hydroxy (or ethoxy) group as well as with the azlactone ring.

When 2-phenyl-4 ethoxymethylen-5-oxazolone is reacted with aniline or piperidine, the principal reaction products are the azlactones (VII, and (VIII), respectively, containing the amine residue instead of the ethoxy group; i.e., in this case the amine reacts with the ethoxy group, not affecting the azlactone ring at all. By-products were formed in each of these reactions in addition to the azlactones (VII) and (VIII). A minute quantity of the piperidide (VI) was formed alongside the azlactone (VIII). The formation of the azlactone (VII) was paralleled by the formation of still another compound, recovered from the mother liquors and having the empirical formula $C_{16}H_{12}O_2N_2$, but having a different melting point than that of the azlactone (VII). At first we thought that this compound and the azlactone (VII) were cis- and trans- isomers. Investigation of their ultraviolet absorption spectra, however, compelled us to abandon this assumption, since the absorption curves of the two compounds were wholly identical. What is more, analysis of the oxazole of the derivatives indicated that their spectra coincided with the spectra of the azlactones of the unsaturated amino acids. This led us to the idea that the compound that is isomeric with the azlactone (VII) is a derivative of an oxazole and should have the structural formula (IX).



(VII)



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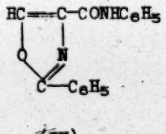


(IX)

It is worthy of note that the azlactones (VII) and (VIII) resist the action of amines. Heating them further with aniline does not rupture the azlactone ring. These azlactones react with alcohol in the presence of sodium alcoholate like other Type (I) lactones, yielding esters of the respective acids.

Study of the ultraviolet spectra of Type (I) azlactones and of the anilides of unsaturated acylated amino acids has been of great value in the present research. An important factor has been the circumstance that our spectra data have enabled us to establish several behavior patterns in the relationship between the position of the maximum in the absorption spectra of these compounds and the nature of the radicals that enter into the molecule of a Type (I) azlactone and of the anilides.

The absorption spectra of the azlactones and the anilides were recorded with a quartz spectrograph and with a Beckmann spectrophotometer. The absorption spectra of the azlactones recorded photographically disclosed several narrow absorption bands of different intensities, whereas the photometric absorption curves of these compounds exhibited only one wide absorption band with a maximum whose position was that of the principal maximum of the spectrogram. The spectra of the anilides did not exhibit separate narrow bands, the curves secured by both methods having a single absorption maximum. The spectra of all the azlactones and anilides were recorded in alcoholic solution, with the exception of 2-phenyl-4-(1-hydroxyethyliden)-5-oxazolone, the spectrum of which can be secured only in an alkaline solution (enol form). The absorption curves of all the tested Type (I) azlactones are alike. Figures 1 and 2 give the absorption spectrum of 2-benzyl-4-benzyliden-5-oxazolone, which is typical of Type (I) azlactones. The absorption curves of all the tested anilides are likewise alike. The absorption curve of one of the anilides tested is given in Fig. 3.

The molecule of a Type (I) azlactone has two systems of conjugated bonds

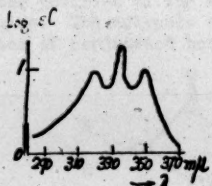


Fig. 1. Absorption spectrum of 2-benzyl-4-benzyliden-5-oxazolone (a quartz spectrograph).

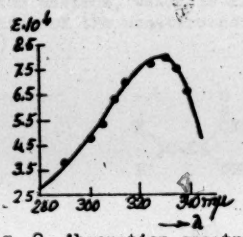


Fig. 2. Absorption spectrum of 2-benzyl-4-benzyliden-5-oxazolone (Beckmann spectrophotometer).

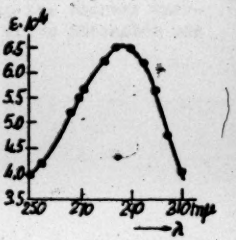


Fig. 3. Absorption curve of the anilide of α-phenacylaminocinnamic acid.

(X). The absorption maximum is located in the 3150-3800 A range in the spectra of the azlactones we tested.

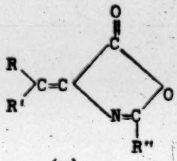
As we see in Table 1, the position of the absorption maximum varies with the changes in the R' and R'' radicals. In the first five azlactones, the R radical is hydrogen or an alkyl group, each having about the same effect upon the position of the maximum. In these azlactones the radical R" is the phenyl group.

TABLE 1

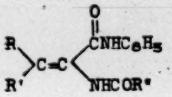
No.	Oxazolones	Formula	Radicals			Absorption max., λ A
			R	R'	R"	
1	2-Phenyl-4-isopropyliden-5-oxazolone	$C_{12}H_{11}O_2N$	CH_3	CH_3	C_6H_5	3150
2	2-Phenyl-4-ethoxymethylen-5-oxazolone	$C_{12}H_{11}O_3N$	H	OC_2H_5	C_6H_5	3270
3	2-Phenyl-4-(1hydroxyethyliden)-5-oxazolone	$C_{11}H_9O_3N$	CH_3	OH	C_6H_5	3300
4	2-Phenyl-4-benzyliden-5-oxazolone...	$C_{16}H_{11}O_2N$	H	C_6H_5	C_6H_5	3650
5	2-Phenyl-4-(1-phenylaminoethyliden)-5-oxazolone.....	$C_{16}H_{12}O_2N_2$	H	NH C_6H_5	C_6H_5	3800
1a	2-Methyl-4-benzyliden-5-oxazolone...	$C_{11}H_9O_2N$	H	C_6H_5	CH_3	3280
2a	2-Benzyl-4-benzyliden-5-oxazolone...	$C_{17}H_{15}O_2N$	H	C_6H_5	$CH_2C_6H_5$	3370
3a	2-Phenyl-4-benzyliden-5-oxazolone...	$C_{16}H_{11}O_2N$	H	C_6H_5	C_6H_5	3650

Only the R' radical varies; R' is methyl in the first azlactone, and the hydroxy (or ethoxy) group, the phenyl group, and the phenylamino group in the other azlactones. The changes in the R' radical were paralleled by a progressive shift of the absorption maximum toward the longer wavelengths. The relationship between the position of the absorption maximum and the nature of the R" radical was discovered in the remaining three azlactones (Table 1, 1a – 3a). In these azlactones, the R and R' radicals remain the same, the R" radical changes. The absorption maximum is located at 3280 A for methyl as the R" group, and at 3650 A for phenyl as the R" group.

The absorption spectra of the anilides of unsaturated amino acids differ from the spectra of the azlactones in the shape of their absorption curves and in the position of the absorption maximum, which is closer to the shorter wavelengths. The molecule of anilides of the unsaturated amino acids possesses one system of conjugated bonds (XI).



(X)



(XI)

The absorption maxima lie in the 2600-3220 A range in the spectra of the tested anilides.

In our study of the anilide spectra we noted the effect of the nature of the R' radical upon the position of the absorption maximum, as we had done on the azlactone spectra.

In the anilides 1, 2, and 5 (Table 2), for example, the R and R" radicals are alike, while the R' radical differs, being the methyl, phenyl, and phenylamino groups, respectively. The absorption maxima of these three anilides range from 2600 to 3220 A. We also endeavored to ascertain the influence

TABLE 2

No.	Anilides	Formula	Radicals			Absorption max λ, A
			R	R'	R"	
1	α-Benzoylamino-β,β-dimethyl-acrylic acid	$C_{18}H_{18}O_2N_2$	CH_3	CH_3	C_6H_5	2600
2	α-Benzoylaminocinnamic acid	$C_{22}H_{18}O_2N_2$	H	C_6H_5	C_6H_5	2815
3	α-Phenacylaminocinnamic acid	$C_{23}H_{20}O_2N_2$	H	C_6H_5	$CH_2C_6H_5$	2850
4	α-Acetylaminocinnamic acid	$C_{17}H_{16}O_2N_2$	H	C_6H_5	CH_3	2840
5	α-Benzoylamino-β-phenylamino-crotonic acid	$C_{23}H_{21}O_2N_3$	CH_3	NHC_6H_5	C_6H_5	3220

of the nature of the R" radical upon the position of the absorption maximum by investigating the anilides 2, 3, and 4, in which the R and R' radicals are alike, while the R" radical is phenyl, benzyl, and methyl, respectively. We found, however, that the absorption maxima of these latter three anilides are very close together. Here we encounter a new factor that influences the relationship between the structure of the azlactones and anilides and the position of the absorption maximum. In studying the spectra of the azlactones we found that the phenyl group in the 2 position and in the 4 position shifts the absorption maximum toward the longer wavelengths.

In the anilides the presence of a phenyl group at the β-position has the same effect, while at the α-position this group has no effect whatever upon the shift of the maximum. Obviously, not only the nature of the radical, but its location with regard to the azlactone or anilide molecule's conjugated bonds as well, governs the displacement of the absorption maximum in the spectra of these compounds. In the azlactones, the radicals at the 2 position directly

adjoin one system of conjugated bonds (X) and adjoin the other system at the 4 position, in both cases setting up the conditions required for an exchange of electrons between the atoms of the phenyl group and the atoms of the azlactone molecule's system of conjugated bonds. Here we observe a change in the position of the absorption maximum. If, instead of the phenyl group, there is an alkyl group without a system of conjugated bonds at these positions, no electron exchange takes place; then we find the maximum to be located at the shorter wavelengths. The phenyl group at the α-position in the anilide molecule does not abut on the sole system of conjugated bonds, so that the necessary conditions for electron exchange are not present; that is probably why this group was found to have no effect upon the position of the absorption maximum.

EXPERIMENTAL

The six Type (I) azlactones listed in Table 3 were used in our study of the reaction of azlactones with amines. These azlactones were prepared by condensing ketones, aldehydes [2], and orthoformic ester [3] with hippuric (or phenaceturic or aceturic) acid in the presence of acetic anhydride.

TABLE 3

No.	Name	Formula	Yield, % of theory	Melting point	Computed %			Found %		
					C	H	N	C	H	N
1	2-Phenyl-4-isopropyliden-5-oxazolone.....	$C_{12}H_{11}O_2N$	60	99-100°	71.64	5.47	6.96	71.66	5.6	7.0
2	2-Phenyl-4-benzyliden-5-oxazolone.....	$C_{16}H_{11}O_2N$	70	165-166	71.50	4.42	5.62	71.35	4.7	5.63
3	2-Benzyl-4-benzyliden-5-oxazolone	$C_{17}H_{13}O_2N$	30-40	105-106	77.53	4.98	5.32	77.81	5.23	5.40
4	2-Methyl-4-benzyliden-5-oxazolone	$C_{11}H_9O_2N$	68	146-148	70.59	4.81	7.49	70.35	5.01	7.51
5	2-Phenyl-4-(1-ethoxymethylen)-5-oxazolone	$C_{12}H_{11}O_3N$	25-30	95-96	66.36	5.10	6.45	66.44	5.05	6.48
6	2-Phenyl-4-(1-hydroxyethyliden)-5-oxazolone	$C_{11}H_9O_3N$	70	193-194	65.03	4.43	6.9	64.81	4.45	6.95

1. Anilide of α-benzoylamino-β,β-dimethylacrylic acid. 5 g of 2-phenyl-4-isopropyliden-5-oxazolone and 2.32 g of freshly distilled aniline were heated to 60-70° for 2 hours with 30 ml of anhydrous benzene in a round-bottomed flask fitted with a reflux condenser. When the reaction was over, the benzene was driven off in vacuum, the remaining crystalline substance being washed with absolute ether to remove any traces of unreacted azlactone and aniline. The anilide of α-benzoylamino-β-β-dimethylacrylic acid is a yellow crystalline substance with a m.p. of 276-278° (with decomposition). It is sparingly soluble in alcohol,

acetone, chloroform, and cold benzene, and somewhat more soluble in pyridine, dioxane, and acetic acid. The yield was 70% of the theoretical.

Found %: C 73.33; H 6.18; N 9.50. $C_{18}H_{18}O_2N_2$. Computed %: C 73.47; H 6.17; N 9.52.

The anilide of α-benzoylamino-β,β-dimethylacrylic acid was hydrolyzed as follows: 1 g of the anilide was boiled with 15 ml of 12% hydrochloric acid for 4 hours. The anilide floating on the surface of the liquid dissolved as heating progressed. When the reaction was over, the mixture was cooled, crystals of benzoic acid, with a m.p. of 121-122°, being thrown down at once. These crystals exhibited no depression when melted with benzoic acid. The benzoic acid was filtered out, and the mother liquor was treated in the cold with bromine water, precipitating the crystals of tribromoaniline. M.p. 119-121°. Yield: 82% of the theoretical.

2. Anilide of α-benzoylaminocinnamic acid. 0.6 g of 2-phenyl-4-benzyliden-5-oxazolone and 0.5 g of aniline were heated with 3 ml of anhydrous benzene to 70° for 2 hours in a round-bottomed flask fitted with a reflux condenser. The solution cleared up within 15 minutes, but then the anilide began to precipitate out gradually. When heating was over, the precipitate was filtered out and washed with a small amount of benzene and then with ether. The yield was 85% of the theoretical. The anilide of α-benzoylaminocinnamic acid is a white crystalline substance with a m.p. of 230-232°. It dissolves when heated in ethyl acetate, though it is insoluble in ether or in cold benzene, its solubility being slight in boiling benzene.

Found %: C 76.58; H 5.53; N 8.23. $C_{22}H_{18}O_2N_2$. Computed %: C 76.30; H 5.20; N 8.38.

3. Anilide of α-phenacylaminocinnamic acid. 0.33 g of 2-benzyl-4-benzyliden-5-oxazolone, 0.24 g of aniline, and 3 g of anhydrous benzene were heated and then processed as set forth in Experiment 2. The anilide of α-phenacyl aminocinnamic acid consists of white flocculent crystals, with a m.p. of 197-198°, that were crystallized from methanol. Yield: 80% of the theoretical.

Found %: C 77.18; H 5.43; N 7.91. $C_{23}H_{20}O_2N_2$. Computed %: C 77.49; H 5.66; N 7.86.

4. Anilide of α-acetylaminocinnamic acid. 0.6 g of 2-methyl-4-benzyliden-5-oxazolone and 0.6 g of aniline were dissolved in 3 ml of anhydrous benzene. Crystals started settling out of the solution in the cold. The reaction mass was heated over a water bath for an hour and then filtered. The precipitate was washed with benzene and with ether and then crystallized from methanol. M.p. 188-190°. Freely soluble in methanol and ethyl alcohol, sparingly in benzene and chloroform. Yield: 73% of the theoretical.

Found %: C 72.79; H 5.39; N 9.98. $C_{17}H_{16}O_2N_2$. Computed %: C 72.86; H 5.75; N 9.96.

5. Anilide of α-benzoylamino-β-phenylaminocrotonic acid. 0.6 g of 2-phenyl-4-(1-hydroxyethyliden)-5-oxazolone, 0.5 g of aniline, and 6 ml of anhydrous benzene were heated together for 2 hours. The resultant anilide was crystallized from ethyl alcohol; m.p. 187-189°. Yield: 55% of the theoretical.

Found %: C 74.12; H 5.90; N 11.42. $C_{23}H_{21}O_2N_3$. Computed %: C 74.36; H 5.70; N 11.32.

Hydrolysis of the anilide of α-benzoylamino-β-phenylaminocrotonic acid: 0.2 g of the anilide was boiled with 10 ml of 18% hydrochloric acid for 4 hours. When the reaction medium cooled, a crystalline precipitate of benzoic acid was

thrown down; it was filtered out. Bromine water was added in the cold to the filtrate until its color remained yellow. Tribromoaniline, with a m.p. of 119-121°, was precipitated. The amount of tribromoaniline thrown down was equivalent to two mols of aniline.

6. Piperidide of α-benzoylamino-β-hydroxycrotonic acid. 0.25 g of 2-phenyl-4-(1-hydroxyethyliden)-5-oxazolone, 0.84 g of piperidine, and 2 ml of anhydrous benzene were heated together to a gentle boil for 2 hours in a round-bottomed flask fitted with a reflux condenser. When the reaction was over, the benzene and the excess piperidine were driven off in vacuum, and a few milliliters of anhydrous ether were added to the residue in the flask. White crystals settled out; they were purified by precipitating them from an alcoholic solution with ether. The piperidide of α-benzoylamino-β-hydroxycrotonic acid consists of white crystals with a m.p. of 140-142° that turn a $FeCl_3$ solution bright blue.

Found %: C 66.51; H 6.82; N 9.81. $C_{16}H_{20}O_3N_2$. Computed %: C 66.63; H 6.89; N 9.72.

7. 2-Phenyl-4-phenylaminomethylen-5-oxazolone. 0.5 g of 2-phenyl-4-ethoxymethylen-5-oxazolone was heated with 0.21 g of aniline and 3 ml of anhydrous benzene for 2 hours in a round-bottomed flask fitted with a reflux condenser. The white crystals of the initial product gradually turned into greenish-yellow crystals, which were filtered out upon completion of the reaction. The precipitate was washed with benzene and recrystallized from acetone or benzene. Recrystallization from benzene yielded acicular greenish-yellow crystals with a m.p. of 158-160°. Yield: 60% of the theoretical.

Found %: C 72.51; H 4.63; N 10.63. $C_{16}H_{12}O_2N_2$. Computed %: C 72.72; H 4.61; N 10.60.

After the substance with a m.p. of 158-160° had been filtered out, the benzene solution was evaporated at room temperature to three-fourths of its original volume, and a substance with a m.p. of 168-170° began to settle out. Its melting point remained the same after recrystallizations from benzene.

Found %: C 72.67; H 4.96; N 10.79. $C_{16}H_{12}O_2N_2$. Computed %: C 72.72; H 4.61; N 10.60.

1 g of 2-phenyl-4-phenylaminomethylen-5-oxazolone and 0.5 g of aniline were heated in 3 ml of anhydrous benzene to 70° for 2 hours. The solvent was driven off, and the residue was washed slightly with ether and recrystallized from benzene. M.p. 158-160°. It exhibited no depression when melted with 2-phenyl-4-phenylaminomethylen-5-oxazolone.

8. Methyl ester of α-benzoylamino-β-phenylaminoacrylic acid. 0.25 g of 2-phenyl-4-(1-phenylaminomethylene)-5-oxazolone was dissolved in 25 ml of methanol to which 1 mg of metallic sodium had been added. The mixture was allowed to stand for several hours at room temperature, white crystals settling out of the solution. The reaction mixture was neutralized and then filtered, the precipitate being washed with a small quantity of methanol. Yield: 41% of the theoretical. The methyl ester of α-benzoylamino-β-phenylaminoacrylic acid consists of white crystals with a m.p. of 182-184°, freely soluble in alcohol and benzene.

Found %: C 68.71; H 5.64; N 9.32. $C_{17}H_{16}O_3N_2$. Computed %: C 68.92; H 5.40; N 9.45.

9. 2-Phenyl-4-(1-piperidylmethylen)-5-oxazolone. 0.5 g of 2-phenyl-4-ethoxymethylen-5-oxazolone, 0.8 g of piperidine, and 2 ml of anhydrous benzene were heated to a gentle boil for 2 hours in a round-bottomed flask fitted with a reflux condenser. As the solution cooled, a certain amount of a white crystalline

substance settled, which was filtered out. The mother liquor was evaporated in vacuum, yellow crystals with a m.p. of 123-124.5° remaining in the distilling flask. They were freely soluble in alcohol, benzene, and ether. Yield 50% of the theoretical.

Found %: C 70.06; H 6.37; N 11.10; $C_{15}H_{16}O_2N_2$. Computed %: C 70.28; H 6.29; N 10.93.

The white substance that settled out of the benzene solution before the latter was evaporated had a m.p. of 338-340° and was the piperidide of α-benzoylamino-β-ethoxyacrylic acid.

Found %: C 67.14; H 6.75; N 8.96. $C_{17}H_{22}O_3N_2$. Computed %: C 67.51; H 7.34; N 9.26.

All the analyses were performed by E.A.Ignatyeva, to whom we are indebted.

SUMMARY

1. Azlactones whose molecules have an alkyl or aryl group as the radical at the 4 position react with amines to yield amides of the respective acids.

2. Azlactones whose molecules have a hydroxy or ethoxy group as the radical at the 4 position react with amines to yield compounds of three types: amides of the respective acids; amides of acids whose hydroxy group has been replaced by the amine radical; and azlactones in which the hydroxy (or ethoxy) group has been replaced by an amine radical.

3. Analysis of the ultraviolet absorption spectra of the azlactones and anilides of unsaturated acylated amino acids enabled us to determine the variation of the position of the absorption maximum with the nature of the radicals and their position with respect to the system of conjugated bonds.

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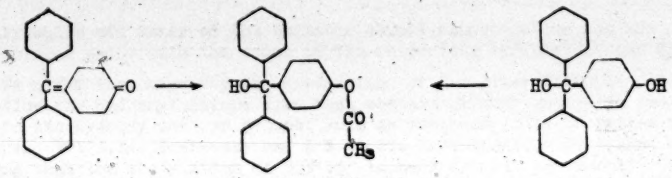
RESEARCHES ON HYDROXYFUCHSONE DYES

XIII. ACETYLATION OF HYDROXYMETHOXYFUCHSONES

I.S. Ioffe

It was noticed a long time ago that when fuchsones are reacted with acetylating agents they react at their quinone ring, finally yielding acetoxytriphenylcarbinols, the latter also being formed during the acetylation of the hydroxytriphenylcarbinols synthesized by preliminary hydration of the respective fuchsones. When unsubstituted fuchsone (I) is acetylated, for instance, we get 4-acetoxytriphenylcarbinol (II), which is likewise prepared by acetylating 4-hydroxytriphenylcarbinol (III).



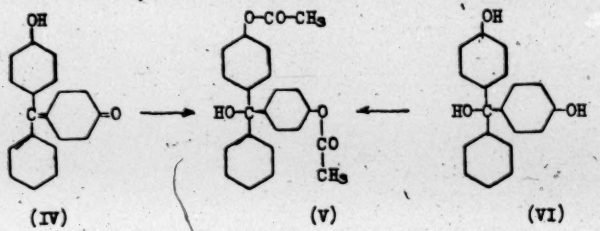
(I) (II) (III)

The presence of an unsubstituted carbinol group in the acetylation products of fuchsones and hydroxytriarylcarbinols is due to the fact that in these compounds that group enters into esterification slowly, while the esters that are formed with its participation are hydrolyzed very readily. The acetoxytriphenylcarbinol was itself synthesized only in an anhydrous medium by reacting triphenyldichloromethane with silver acetate. It has been found [2] that this ester is readily hydrolyzed by water to triphenylcarbinol.

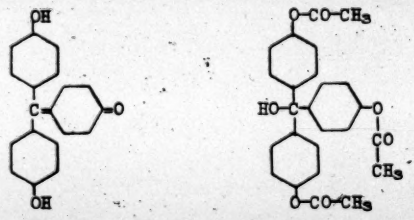
Because of the foregoing, the acetylation of hydroxyfuchsone dyes involves both the hydroxy group of the dye and its quinoid ring, yielding the corresponding polyacetoxytriphenylcarbinols. Benzaurin (IV) yields [3] 4,4'-diacetoxytriphenylcarbinol (V) in a reaction of this sort, though we have also synthesized the latter [4] by acetylating 4,4'-dihydroxytriphenylcarbinol (VI): (see Scheme 1, following page).

Similarly, aurin (VII) yields 4,4',4''-triacetoxytriphenylcarbinol (VIII), as described by Gomberg [5]: (see Scheme 2 following page).

All these acetoxytriphenylcarbinols are readily saponified by treating them with mineral acids or alkalies. When they are reacted with acids, colored onium salts of the respective fuchsone compounds are formed [6]. When they are reacted with alkalies, salts of the hydroxy triarylcarbinols are formed, which



(IV) (V) (VI) (Scheme 1)



(VII) (VIII) (Scheme 2)

usually split off water at the suitable alkali concentration and are converted into colored salts with the anion of the respective hydroxyfuchsone dye.

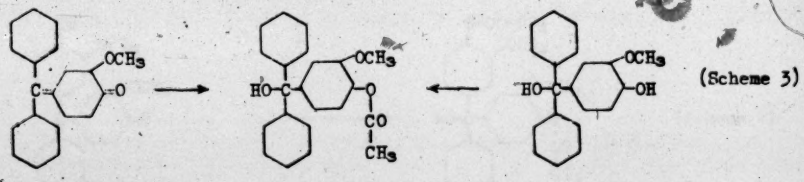
We might have expected the acetylation of the other fuchsone derivatives, including the hydroxyfuchsone dyes that contain methoxy groups in the ortho position to the hydroxy and oxo groups, such as rubrocol (XIV) to follow the same pattern. But I.Ya. Postovsky and A M.Eidlin have recently published a paper [7] stating that the acetylation of 3,3',3"-trimethoxyaurin (rubrocol) results in the formation of a colorless acetyl derivative with a m.p. of 206-208°, which is saponified into a new colorless substance with a m.p. of 238-240° instead of into a salt of the initial dye. This led Postovsky and Eidlin to conclude that the methoxy group causes the acetylation of methoxyfuchsone derivatives to follow an unusual course for fuchsone compounds, ending up in the formation, not of the respective acetoxytriarylcarbinols, but rather of more complex substances that cannot be converted by saponification into the original fuchsone derivative.

Our investigations have demonstrated, however, that methoxyfuchsone derivatives can be acetylated in the manner applicable to all fuchsone derivatives, resulting in the formation of the corresponding acetoxytriarylcarbinols.

The parent of our methoxyfuchsone compounds was 3-methoxyfuchsone (IX), investigated in detail by us together with Z.Ya.Khavin [8]. Acetylating this substance, we secured 3-methoxy-4-acetoxytriphenylcarbinol (X), which was also synthesized by acetylating 3-methoxy-4-hydroxytriphenylcarbinol (XI): (see Scheme 3, following page).

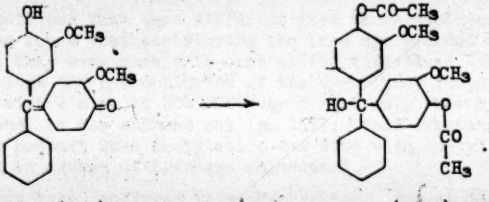
The acetyl derivative (X) crystallizes as colorless crystals with a m.p. of 129-131°. When it is heated with alkalies, we get a salt of the hydroxycarbinol (XI), from which the original fuchsone can be secured by acidulation and dehydration.

From a more complex methoxyfuchsone compound, 3,3' dimethoxybenzaurin (XII), we secured [8] an acetylation product with a m.p. of 129°, to which we



(IX) (X) (XI) (Scheme 3)

assigned the acetoxycarbinol structure (XIII):

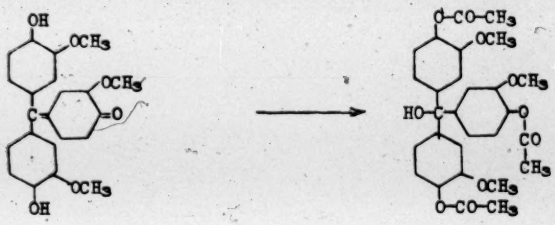


(XII) (XIII)

After learning of the paper by Postovsky and Eidlin [7], we decided to return to this substance and make a more thorough study of it. A more thorough purification, plus repeated recrystallization, yielded the acetylation product of 3,3'-dimethoxybenzaurin in the form of colorless crystals with the constant m.p. of 136-138°. This substance is saponified fairly readily by acids as well as by alkalies. When it is heated with hydrochloric acid, we get the hydrochloride of the original dye; when heated with an alkali, the substance gradually dissolves, coloring the solution the characteristic blue of alkaline salts of dimethoxybenzaurin. Alcoholic solutions of the acetyl derivative are saponified most readily. Colorimetric determinations show that the acetyl derivative is quantitatively converted into a salt of the dye when such an alcoholic solution is treated with alkali. When the acetyl derivative is heated with zinc in acetic acid, it is reduced, being converted into a derivative of acetoxytriphenylmethane. Determination of the number of acetyl groups in the acetyl derivative yields results that indicate the presence of 2 acetoxy groups, while the results of combustion analysis agree with the structure (XIII).

Our new researches have, therefore, fully confirmed that 3,3'-dimethoxybenzaurin (XII) is acetylated in the usual manner for fuchsone compounds, yielding the acetyl derivative of an acetoxytriphenylcarbinol structure (XIII). We were able to show that a product of similar structure and properties is formed when rubrocol (XIV) is acetylated. The resulting acetyl derivative crystallizes from alcohol as colorless crystals with a m.p. of 156-158°. It is also readily and quantitatively saponified by acids and alkalies, yielding salts of the original rubrocol. It is reduced when heated with zinc in acetic acid, yielding an acetyl derivative of leucorubrocol. Determination of the acetyl groups and the ultimate analysis demonstrated that our acetylation product of rubrocol doubtless has the structure of the acetoxytriphenylcarbinol derivative (XIV): (see Scheme 4, following page).

But, as we have said, Postovsky and Eidlin secured an altogether different product, with a m.p. of 206-208°, when they acetylated rubrocol, which did not yield the original dye upon saponification. We deliberately acetylated the



(XIV) (XV) (Scheme 4)

rubrocol under conditions that were different from those employed by Postovsky and Eidlin. Having found that acetylating the free dye yielded amorphous substances from which they were unable to crystallize individual substances, these researchers acetylated the hydrochloride of the dye. They found that their acetyl derivative with a m.p. of 206-208° was formed only when hydrogen chloride was present, and, as the authors say (p. 151); "this substance became the principal reaction product when acetylation was done with acetyl chloride, i.e., in a medium having an excess of hydrogen chloride."

Our experiments have confirmed this observation. But at the same time we noted that when rubrocol was acetylated under any conditions whatsoever, the crude reaction product, which was precipitated in a colorless, though amorphous, form when the acetylated mixture was diluted with water, turned the characteristic violet of alkaline salts of rubrocol when it was acted upon by an alkali. This indicates that the acetylation of rubrocol also yields the products of the usual fuchsone reaction, which are reconverted into the original dye by saponification. When it is acetylated under conditions in which the reaction medium contains hydrogen chloride, the yield of these products is low, so that we decided to carry out the reaction under conditions that would exclude the presence of hydrogen chloride altogether in order to secure these very acetylation products, acetylating free rubrocol with acetic anhydride and anhydrous sodium acetate. The resulting crude acetylation product actually was an amorphous precipitate with an extremely low melting point, melting even in hot water and turning into a tacky, tarry mass. Direct crystallization of such a product was unsuccessful. But treating this substance with ether washed out the impurities that blocked crystallization. The residual light-gray powder, which was sparingly soluble in ether and melted above 100°, crystallized readily from alcohol. Using this method of purification, we were able to secure the acetyl derivative (XV) described above, as crystals with the constant m.p. of 156-158°, the yield exceeding 60% of the theoretical.

In seeking methods of purifying this substance, we noticed that the crude acetylation product of rubrocol, precipitated directly when the acetylating mixture was diluted with water, was very highly soluble in ether, even in a minute quantity of the latter. But when the filtered ether solution stood for a long time or – better yet – when it was evaporated, a light precipitate settled out, which was only sparingly soluble in ether and could be readily crystallized from alcohol. This observation enabled us to employ still another variant of isolating the rubrocol acetylation product, which was simpler to carry out and gave us even higher yields of the reaction end product.

Our investigations have therefore shown that, contrary to what Postovsky and Eidlin thought, rubrocol is acetylated in the usual manner for fuchsone compounds, yielding an acetoxytriphenylcarbinol derivative (XV), which is reconverted into a salt of the original dye by saponification with an acid of an

alkali. We also found that acetylation in the presence of hydrogen chloride causes the reaction to follow two paths, finally resulting in the formation of two substances, the quantitative proportions of which depend upon the reaction conditions, chiefly the percentage of hydrogen chloride present. Alongside the normal acetylation product with a m.p. of 156-158° (XV), there is formed the substance described by Postovsky and Eidlin, with a m.p. of 206-208°, which is not reconverted into the original rubrocol by saponification. These two substances have different solubilities in alcohol; this fact may be employed in their separation.

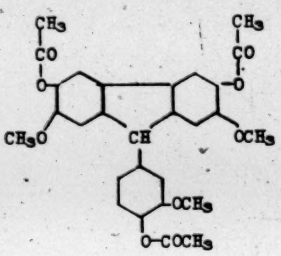
We have found that the reaction with 3,3'-dimethoxybenzaurin (XII) is similar. When this dye is acetylated in the presence of hydrogen chloride, there is formed – in addition to the acetylation product described above, with a m.p. of 136-138°, which follows the path that is customary for the fuchsones and is reconverted into the original dye by saponification – a smaller quantity of some other substance that is much less soluble in alcohol, crystallizes from alcohol as colorless crystals with a m.p. of 229-232°, and does not yield the original dye when saponified, but another, colorless substance that melts at 199-201° after first turning green.

What are the substances secured in the acetylation of hydroxyfuchsone dyes that are not reconverted by saponification into the original dyes?

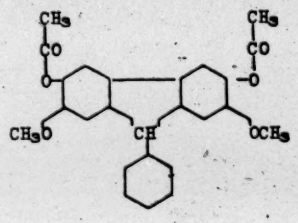
When these substances are acetylated they yield only methoxyfuchsone dyes, and the acetylating mixture has to contain hydrogen chloride. As Postovsky and Eidlin have stated and as our experiments have confirmed, hydroxyfuchsone dyes that do not contain a methoxy group yield nothing but the acetylation products that are normal for the fuchsones no matter what the reaction conditions. But, as we have shown [1], when methoxyfuchsone dyes are heated with mineral acids, they undergo specific transformations that result in the irreversible formation of isomeric hydroxy compounds, which apparently possess a mesophenylfluorene structure. When 3,3'-dimethoxybenzaurin is heated with hydrochloric acid, for instance, a colorless substance of the same empirical composition, melting at 199-201° after first turning green, is formed; correspondingly, the mixture of products of the acid transformations of rubrocol yield a colorless substance that fuses at 238-240° after first turning green.

But these are precisely the substances secured by saponifying the "anomalous products" of acetylating 3,3'-dimethoxybenzaurin and rubrocol. On the other hand, when the products of the acid isomerization of these dyes described previously [1] are acetylated, substances are formed that are the same as the substances described above, secured when these dyes are acetylated in the presence of hydrogen chloride. This indicates that the substance with a m.p. of 206-208°, synthesized by Postovsky and Eidlin when they acetylated rubrocol in the presence of hydrogen chloride, and the substance with a m.p. of 229-232° that we secured when we acetylated 3,3'-dimethoxybenzaurin under similar conditions are not products of the direct acetylation of the original dyes, but are formed in the acetylating medium as the result of a preliminary acidic isomerization of these dyes by the hydrogen chloride, followed by the acetylation of the colorless hydroxy compounds, produced by this isomerization. As has been pointed out in our previous report [1], it is most probable that the latter compounds have a mesophenylfluorene structure. We therefore believe that these substances with m.p. of 206-208° and 229-232° have the following structures: (XVI) for the first, and (XVII) or (XVIII) for the second: (see Scheme 5, following page).

This conclusion contradicts the arguments advanced by Postovsky and Eidlin [7]. The latter authors assumed that the substance with a m.p. of 206-208°

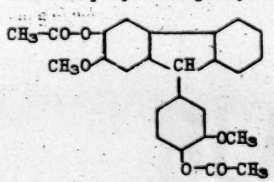


(XVI)

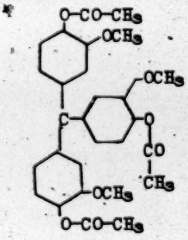


(XVII)

that they had secured by acetylating rubrocol in the presence of hydrogen chloride was a dimer of the free radical (XIX), with a so-called Chichibabin structure of the benzhydryltetraphenylmethane type.



(XVIII)



(XIX)

The arguments cited by Postovsky and Eidlin in support of their conclusions are unconvincing. One of their arguments is based upon the circumstance that the substance with a m.p. of 206-208° they had secured from rubrocol exhibited no active hydrogen in a Tserevitinov-Chugaev reaction. On the other hand, this substance remains unchanged during reduction, whereas the reduction of acetoxytriphenylcarbinols converts them into acetoxytriphenylmethane derivatives.

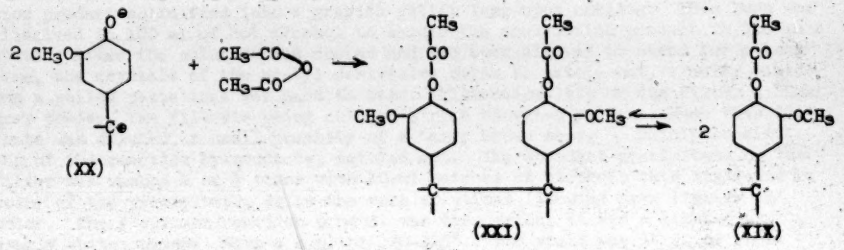
We can corroborate these observations. Nor does the substance with a m.p. of 229-232° that we secured by acetylating 3,3'-dimethoxybenzaurin in the presence of hydrogen chloride manifest any active hydrogen, and it, too, remains unchanged during reduction. Yet these properties, while they do show that these substances are not derivatives of acetoxytriphenylcarbinol, still do not prove that they are dimers of Type (XIX) free radicals. The acetoxymesophenylfluorenes (XVI) and (XVII) or (XVIII) must also possess these properties.

Nor is the argument based on molecular weight determinations convincing. The authors themselves do not give quantitative data, but confine themselves to the assertion (p. 154) that "no constant values were obtained in determining the molecular weight in camphor, by the Rast method; in most of the cases the results were lower than those calculated for the dimer, though considerably higher than those for the monomer. Apparently, dissociation occurred..." Precise results could not have been expected, however, when the molecular weight of such substances was determined by the Rast method. We measured [1] the molecular weight of the acidic isomerization products of methoxyfuchsone compounds we had synthesized and of their acetyl derivatives cryoscopically, securing results

that clearly demonstrated the monomeric composition of these substances.

The combustion results cited by Postovsky and Eidlin are completely unexpected. In computing the elementary composition of the substance with a m.p. of 238-240° that they had secured by acetylating rubrocol and then saponifying the acetyl derivative, they assumed (p. 155) that this substance had the empirical formula of $(C_{22}H_{21}O_6)_2$. The empirical formula of rubrocol is $C_{22}H_{20}O_6$, however. In other words, when they acetylated rubrocol and then saponified the acetyl derivative (without any reducing agent present!), they secured a substance that was allegedly richer in hydrogen. As we see it, this substance is merely a product of the isomerization of rubrocol and has the same empirical formula $C_{22}H_{20}O_6$. The analysis results are equivalent to the formula $C_{22}H_{21}O_6$ or that of $C_{22}H_{20}O_6$, within the limits of experimental error.

The reason for the foregoing becomes clear when we analyze the mechanism for the formation of the hypothetical dimer of the free radical (XIX) advanced by Postovsky and Eidlin [7]. According to them, in one of rubrocol's mesomeric forms, illustrated by them schematically (p. 151) by the formula (XX), it reacts with acetic anhydride, adding acetyl radicals to the negatively charged oxygen atoms and being converted into a hexaphenylethane derivative (XXI), which dissociates to yield the free radical (XIX). They represent these transformations by the following diagram (p. 152):



(XX) (XXI) (XIX)

As Postovsky and Eidlin see it, the resulting free radical is dimerized by the hydrogen chloride, yielding a substance whose structure is that of a Chichibabin compound. They consider the substance with a m.p. of 206-208° that they secured when they acetylated rubrocol to be a substance of that kind.

The diagram proposed by Postovsky and Eidlin places us in a quandry, however. As we see from the diagram, two acetyl radicals of acetic anhydride are added to 2 molecules of fuchsone. But what does the anhydride's oxygen atom attach itself to then? For the authors stress (p. 151) that they carried out the acetylation reaction without any reducing agent present. Nor is it difficult to realize that neither the hexaphenylethane derivative (XXI) nor the free radical (XIX) can be formed when acetyl chloride is used as the acetylating agent, so that the formation of the benzhydryltetraphenylmethane derivative is likewise out of the question.

It follows from the foregoing that the assertions of Postovsky and Eidlin regarding the course of the interaction of rubrocol with acetylating agents and the structure of the resultant substances cannot be regarded as well-founded.

Our researches lead us to conclude that methoxyfuchsone dyes are also acetylated in the manner that is typical of fuchsone compounds, yielding acetyl derivatives with an acetoxytriphenylcarbinol structure that are reconverted into the original dye by saponification. Acetylation of the same dyes with hydrogen

chloride present in the reaction medium results in an irreversible acidic isomerization to colorless hydroxy compounds that is characteristic of these dyes, with, most likely, a mesophenylfluorene structure. These latter hydroxy compounds are acetylated in a secondary reaction, yielding acetyl derivatives that are not reconverted into the original dyes by saponification, of course, but into colorless products of the acidic isomerization of the latter.

EXPERIMENTAL

I. Acetylation of 3,3'-Dimethoxybenzaurin by Acetic Anhydride

Synthesis, recovery, and purification of the acetylation product. 16.7 g of 3,3'-dimethoxybenzaurin was dissolved in 100 ml of acetic anhydride in a 500-ml flask fitted with a reflux condenser and a dropping funnel. 20 g of anhydrous sodium acetate was added to the solution, and the resulting suspension was boiled for 6 hours, the solution turning light-yellow and remaining that color throughout the boiling period. Then 40 ml of water was cautiously added to the solution a drop at a time, while boiling continued, in order to decompose the acetic anhydride and dissolve the sodium acetate. The resultant solution was poured into 1 liter of hot water, the reaction product settling as a tacky, viscous mass, which was separated out and washed repeatedly with water. The reaction product solidified into a grayish yellow lump upon cooling. This lump was dissolved in 100 ml of hot alcohol to secure the acetylation product in the pure state. After the solution had cooled and had been allowed to stand for a long time, the crystals of the acetyl derivative began to settle out, finally yielding a yellow paste that was hard to stir. Filtration left on the filter a light-gray powder, the filtrate being colored a rich brownish yellow. When this filtrate was diluted, a small quantity of a tarry brown mass, mainly consisting of the reaction by-products, settled out. The abundant precipitate on the filter was washed 2 or 3 times with 10-ml batches of alcohol; this lightened the color of the precipitate, while the wash solutions likewise grew lighter in color. The resultant reaction product was then dried; it was a light-gray, nearly white, powder, with a m.p. of 120-125°. Its yield was 14 g, or about 65% of the theoretical. Several recrystallizations from alcohol yielded wholly colorless crystals with a constant m.p. of 136-138°.

Properties of the acetylation product. The acetylation product is insoluble in water, sparingly soluble in ether; slightly soluble in cold alcohol, very readily soluble in hot alcohol, and freely soluble in glacial acetic acid. It crystallizes from alcohol as colorless crystals with a m.p. of 136-138°. When an ether solution is slowly evaporated, it settles out as fine needles with the same melting point. Its solutions in all organic solvents are colorless, remaining so even when heated for a long time. When an aqueous suspension of the substance is heated with mineral acids, the precipitate turns violet, the solution turning the same color. When an aqueous suspension of the substance is treated with an alkali, it dissolves (solution occurring more quickly when heated), the solution being colored blue.

Saponification is accelerated when an alcoholic solution of the acetyl derivative is employed. When aqueous alkali was added to such a solution, it at first turned cloudy, but the subsequent precipitate rapidly dissolved, the solution turning blue, as stated above, when heated. When an aqueous-alcoholic solution was heated, saponification took place in a few minutes.

The appearance of the solution remained unchanged when the acetyl derivative was dissolved in acetic acid and boiled for a long time, but the precipitate thrown down when the filtered solution was diluted no longer was colored by the addition of acids or alkalies. When heated with alkalies, it entered

solution, the solution remaining colorless.

0.1204 g substance: 0.3052 g CO_2; 0.0612 g H_2O. 0.1264 g substance: 0.3203 g CO_2; 0.0643 g H_2O. Found %: C 69.10, 69.06; H 5.65, 5.68. $C_{25}H_{24}O_7$. Computed %: C 68.81; H 5.5.

Preliminary saponification of the substance with alkali, followed by addition of sulfuric acid, proved to be more convenient for the quantitative determination of the number of acetyl groups it contained. A weighed sample of the substance was heated with 4 ml of 5% sodium hydroxide, after which 10 ml of 10% sulfuric acid was added and the acetic acid was driven off with steam, 0.5 liter of the distillate being taken for titration.

0.2604 g substance: 12.10 ml 0.1 N NaOH. 0.2182 g substance: 9.80 ml 0.1 N NaOH. Found %: CH_3CO groups: 19.88, 19.32. $C_{21}H_{18}O_5(CH_3CO)_2$. Computed %: CH_3CO groups 19.72.

Determination of the hydroxyfuchsone dye. 0.0436 g of the substance was dissolved in 10 ml of alcohol, and 10 ml of 1% sodium hydroxide was added, after which the mixture was heated for 1 hour over a water bath. The resulting solution was placed in a measuring flask, and distilled water was added until the total volume was 1 liter. At the same time a standard solution was prepared by dissolving 0.0334 g of 3,3-dimethoxybenzaurin in 1 liter of 0.01% sodium hydroxide. Colorimetric comparison indicated that the color intensity of the standard and test solutions was exactly alike.

II. Acetylation of 3,3'-Dimethoxybenzaurin by Acetyl Chloride

Synthesis, separation, and purification of the reaction products. 9.5 g of 3,3'-dimethoxybenzaurin hydrochloride was placed in a flask fitted with a reflux condenser, and a mixture of 40 g of acetic anhydride and 20 g of acetyl chloride was added. The dye dissolved partially, turning the solution the crimson color that is typical of the onium salt. The resulting suspension was boiled until all the dye dissolved and the color vanished. The reaction was accompanied by the evolution of hydrogen chloride gas. The final solution was transparent and light-yellow. It was poured into 0.5 liter of water, and the mixture was stirred until all the acetic anhydride and acetyl chloride had been decomposed. This yielded a low-fusible mass that solidified when cooled. The mass was filtered out, washed repeatedly with water, and pulverized in a mortar, the resulting powder being rewashed with water and filtered. The crude reaction product dissolved readily and completely in hot alcohol. When alkali was added to a drop of the alcoholic solution, it turned blue, the color of an alkaline solution of 3,3'-dimethoxybenzaurin.

The whole of the acetylation product was dissolved in 50 ml of alcohol h heated to the boiling point. As the solution cooled, a light-gray powder settled out; it was filtered out, squeezed out well on the filter, and washed twice with 10 ml batches of alcohol. The resultant precipitate was no longer fully soluble in hot alcohol; when this precipitate was boiled with 50 ml of alcohol, a small quantity of a colorless precipitate remained, which was filtered out. It weighed about 1 g after drying. M.p. 200-205°. It dissolved with difficulty in hot alcohol and was recovered as colorless crystalline needles with a m.p. of 229-232° by recrystallization from the alcohol. When this substance was boiled with alkali, it dissolved, yielding a colorless solution. This may be employed as a test for determining the purity of the substance. The appearance of even a pale light-blue color when the substance is heated with alkali is an indication that a trace of the normal acetylation products is present and proves that further recrystallization is needed. All the properties of the resultant compound and of the acetylation product of the substance formed during

during the acidic isomerization of 3,3'-dimethoxybenzaurin and described in our preceding paper [1] are alike. A mixture of the two likewise fused at 229-232°.

When the filtrates were chilled for a long time, a different substance settled out, which yielded a blue color when dissolved in alkali. Several recrystallizations yielded 3-4 g of this substance as colorless crystals that had a sharp melting point at 136-138°. A mixture of this substance with the product of the normal acetylation of 3,3'-dimethoxybenzaurin described above had the same m.p.

Comparison of the properties of the reaction products. The crystalline substance with m.p. 136-138° is rapidly saponified when heated with aqueous alkali, dissolving and turning the solution blue; the substance with a m.p. of 229-232° is saponified much more slowly by aqueous alkali, the solution remaining colorless. The substance with m.p. of 136-138° dissolves very readily in hot alcohol and crystallizes from small volumes of this solvent; the substance with a m.p. of 229-232° is sparingly soluble even in boiling alcohol, and large quantities of the solvent are required for its crystallization. The substance with a m.p. of 136-138° turns violet when heated with 10% hydrochloric acid, the solution turning crimson; the substance with m.p. of 229-232° is unchanged when heated with hydrochloric acid.

III. Acetylaction of 3,3',3" -Trimethoxyaurin (Rubrocol) By Acetic Anhydride

Synthesis, recovery, and purification of the reaction product. 19 g of free rubrocol, 20 g of anhydrous sodium acetate, and 100 ml of acetic anhydride were placed in a 500-ml flask fitted with a reflux condenser and a dropping funnel. The resulting suspension was boiled for 6 hours, after which 40 ml of water was cautiously added drop by drop, without interrupting the boiling, and the acetic-acid solution was poured into 0.5 liter of water. This threw down a low-fusible precipitate, which solidified into a tacky, resinous mass upon cooling; the latter was separated from the solution, washed several times with warm water, and dried. The reaction product was then triturated in a mortar with 50 ml of ether. The mass, which was tacky at first, gradually turned into a light-gray powder that was sparingly soluble in ether; as the latter dissolved the impurities, it turned brownish-yellow. The precipitate became nearly colorless after it was filtered out of the ether and washed on the filter with the same solvent. It had a melting point of 105-115° after drying and weighed about 16 g (60% of the theoretical).

In another variant, the reaction mixture was chilled and poured into a 1-liter separatory funnel immediately after it had been produced by acetylation and decomposition of the acetic anhydride by water. 0.5 liter of water was added, and the whole was chilled and then agitated with ether until the tarry product thrown down when the mixture was diluted with water dissolved in the ether completely. The ether layer was removed, washed with water, and filtered (all these operations must be done quickly). The filtered solution (about 100 ml of ether) was allowed to stand in a dish until all the ether had been eliminated. A light-gray precipitate was left, which was pulverized, wetted with ether, and filtered to separate it from the yellow ether mother liquor. Washing it on the filter with ether yielded a light precipitate, which was dried. Weight: about 18 g.

By now the reaction product crystallized satisfactorily from alcohol, no matter how it was recovered. Repeated recrystallization yielded wholly colorless crystals with a constant m.p. of 158°.

Properties of the acetylation product. It is insoluble in water, very sparingly soluble in ether, somewhat more soluble in cold alcohol, and readily soluble in hot alcohol, crystallizing from the latter as colorless crystals with a m.p. of 156-158°. It is soluble in benzene and in acetic acid. The solutions in organic solvents remain colorless when boiled. The substance is readily

saponified by mineral acids and by alkalies, being most rapidly saponified in alcoholic solutions. When hydrochloric acid is added to the latter, the solution turns violet, the color that is characteristic of an onium salt of rubrocol. Saponification is quantitative when the reaction with alkali is carried out in an alcoholic solution. When the substance is boiled for a long time with zinc in acetic acid, it is reduced; the product secured when the filtered solution is diluted is no longer colored by the addition of a mineral acid or an alkali.

0.1319 g substance: 0.3121 g CO_2; 0.0696 g H_2O. 0.0861 g substance: 0.2029 g CO_2; 0.0439 g H_2O. Found %: C 64.53, 64.26; H 5.90, 5.68. $C_{28}H_{28}O_{10}$. Computed %: C 64.12; H 5.34. 0.2624 g substance: 15.1 ml 0.1 N NaOH. 0.2650 g substance: 15.2 ml 0.1 N NaOH. Found %: CH_3CO groups 24.74, 24.36. $C_{22}H_{19}O_7(CH_3CO)_3$. Computed %: CH_3CO groups 24.62.

Determination of the dye. 0.0524 g of the substance was dissolved in 10 ml of alcohol, and 10 ml of 1% sodium hydroxide was added to the solution, after which the mixture was heated for one hour over a water bath. The resultant solution was brought up to one liter in a measuring flask by adding distilled water. At the same time 0.0380 g of rubrocol was dissolved in 1 liter of 0.01% sodium hydroxide. Comparison in a colorimeter indicated that the colors of the test and the standard solutions had the same intensity.

IV. Acetylation of 3,3',3'-Trimethoxyaurin by Acetyl Chloride

Synthesis, separation, and purification of the reaction products. 10 g of rubrocol hydrochloride, 40 g of acetic anhydride, and 20 g of acetyl chloride were placed in a flask fitted with a reflux condenser. The solution turned violet. The resulting suspension was boiled until all the deposit dissolved and the violet color disappeared. The resulting yellow solution was poured into 0.5 liter of water and stirred until all the acetic anhydride and acetyl chloride decomposed, the reaction product settling out as a light-yellow powder, which was beaten into a tacky lump. The latter was separated from the solution and washed several times with warm water. The resultant substance was readily soluble in warm alcohol. When a drop of its alcoholic solution was placed in a sodium hydroxide solution, it turned the latter an intense violet. The crude reaction product was crystallized from 50 ml of hot alcohol. As thelatter cooled, a crystalline colorless precipitate settled out, which was converted into a violet solution by processing with alkali. Only after several recrystallizations from alcohol did we secure crystals that did not yield colored solutions when heated with alkali; they had a constant m.p. of 206-208°, and their yield was 4 g.

When the basic mother liquor was allowed to stand for a long time, a crystalline precipitate settled out; it was filtered out and recrystallized repeatedly from alcohol, after which it had a sharp m.p. at 156-158°. A mixture of this substance with the rubrocol acetylation product described above also fused at 156-158°. The yield of the crystalline product was about 1 g.

Comparison of the synthesized substances. The properties of the substance with a m.p. of 206-208° are the same as those of the substance described by Postovsky and Eidlin. It is practically unaffected by heating with mineral acids, while it dissolves when boiled with an aqueous, or, better yet, an aqueous-alcoholic alkali, the solution remaining colorless; the substance with a m.p. of 156-158° is saponified much more easily, yielding (as has been said) solutions that exhibit the colors of rubrocol salts. The substance with a m.p. of 206-208° is much less soluble in alcohol than the substance with a m.p. of 156-158°. The substance with a m.p. of 206-208° proved to be the same substance as the one secured by acetylating the product of the acidic isomerization of rubrocol described previously [1].

*Heating with alkali yields the violet solution that is characteristic of alkaline salts of rubrocol.

SUMMARY

1. Contrary to the notions advanced by Postovsky and Eidlin [7], hydroxyfuchsone dyes that contain methoxy groups at the ortho position to the hydroxy or oxo groups are acetylated in the manner that is usual for hydroxyfuchsones, yielding the respective acetoxytriphenylcarbinols.

2. When these acetyl derivatives are treated with mineral acids or alkalies, they are saponified, yielding colored salts of the original hydroxyfuchsone dyes.

3. When these methoxyfuchsone dyes are acetylated in the presence of hydrogen chloride, the reaction follows two courses, the relative rates depending upon the amounts of hydrogen chloride present. In one, the acetylation products that are typical of the fuchsones are formed, which are converted by saponification into salts of the original dyes; in the other, an acidic isomerization of the original dyes [1] takes place in the reaction medium, followed by acetylation of the hydroxyfluorene compounds that are apparently formed. Saponification of these substances does not reconvert them into the original dyes, but into the indicated colorless products of their acidic isomerization.

4. Postovsky's and Eidlin's idea [7] that these products of the "anomalous acetylation" of methoxyfuchsone dyes are dimers of free radicals, with the structure of Chichibabin compounds, does not accord with reality.

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* See C.B. Translation p. 508.
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AZO DYES FROM 1,5 AMINONAPHTHOL AND SOME OF ITS DERIVATIVES

VIII. RESEARCH ON THE ABSORPTION SPECTRA OF SOME INTERMEDIATES AND AZO DYES OF THE NAPHTHALENE SERIES*

V. V. Perekalin and M. V. Savostyanova

In studying the reaction of 1,5-aminonaphtholsulfo acids with diazo compounds we have synthesized a series of azo dyes. In order to shed some light on the complicated picture of the absorption spectra of numerous azo dyes we made a systematic investigation of the absorption spectra of a number of compounds of the naphthalene series that contained, individually or in various combinations, the substituents entering into the composition of the azo dyes synthesized from 1,5-aminonaphtholsulfo acids. The absorption spectra of 21 out of the 28 substances tested have been measured for the first time, among them being: 1,5-aminonaphthol; its sulfo acids (the 2-, 4-, 6-, 7-, and 8-1,5-aminonaphtholsulfo acids); 1-benzeneazonaphthalene; and the azo dyes secured from 1,5-aminonaphthol and the 1,5-aminonaphtholsulfo acids.**

The immediate objectives of this research have been: 1) determining the exact nature of the absorption spectra, i.e., the shape of the individual maxima throughout a large wavelength range (from 210 to 600 mμ); 2) discovering wherever possible the relationship between the position of all the maxima (not only the longwave ones, as is usually done) and the structure of the substances investigated. We felt that this job deserved doing, for in the overwhelming majority of cases only the longwave maxima are considered in investigating the relationships between the nature of absorption and molecular structure, the other, shortwave maxima of the absorption spectrum being ignored.

We know of only isolated papers dealing with the relationship between the structure of organic compounds and the various absorption bands of their spectra. There is some comment on this problem in the papers by Hartley [1], for example. Then, as far back as 1910, A.E.Porai-Koshits commented on the difference between the bands produced by general conjugations all along the molecule and those produced by partial conjugated systems [2]. The relationship between the types of absorption bands in the spectra of plane or nearly plane molecules and the electron oscillations along mutually perpendicular axes was established much later [3]. Research on the relationship of the various maxima to the structure of the molecule is therefore still in an embryonic stage.

1. Method of Investigating Absorption Spectra

All the substances we investigated were first purified specially.*** We

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* We wish to express our gratitude to Prof. T.P.Kravets for his permitting us to use his instrument.

** The synthesis of these azo dyes will be described in our next report.

*** See * following page.

investigated the absorption of aqueous and alcoholic solutions of neutral molecules, as well as of their sodium and hydrochloric salts, dissociated into anions and cations. Most of the substances in which we were particularly interested (1,5-aminonaphthol; the sulfo acids of 1,5-aminonaphthol; and the azo dyes derived from the latter) were readily soluble in water as their sodium salts and nearly insoluble in other solvents (particularly non-polar ones), so that we used water as our solvent. Whenever the compound under test was insoluble in water, the latter was replaced by another polar solvent – alcohol. The concentrations of the solutions were recomputed as molar concentrations, so that all the measurements were made, as far as possible, under identical conditions. This enabled us to make use of comparable observation values with some confidence.

The absorption spectra were recorded by means of photoelectric photometry, using the SF-11 quartz spectrophotometer. The optical density ($D\lambda$) and the molar extinction coefficient (ε)* were measured with an accuracy of a fraction of one per cent [4]. In several organic compounds the width of the absorption band was a few mμ. With a band of that width the size of the spectrum section passed by the instrument (the effective width of the slit, $\delta\lambda$), which has a substantial effect upon the accuracy of determination of the shape of the curve and the value of ε, should be of the order of 0.1 mμ. In the instrument available to us $\delta\lambda$ was about 1 mμ in the 300 mμ region. In some instances, therefore, (in recording the spectra of 1-naphthol, 1-naphthylamine, 1-naphthalenesulfo acid, 1,5-aminonaphthol, the latter's sulfo acids, and the azo dyes synthesized from 1-naphthol and 1,5-aminonaphthol), we supplemented this with a photographic method, which yielded a qualitative picture of absorption, enabling us to judge whether fine structure was present or not. The width of the fine-structure bands recorded in the photographs was such for some substances, however, that all these bands were discovered on the curve plotted with the instrument [5], provided the measurements were made carefully (at intervals of 1 mμ). These comments justify our asserting that the Beckmann instrument makes it possible to make measurements with a high degree of accuracy and to solve the problem we had set ourselves, with negligible errors.

2. Description of the Absorption Spectra

a) Intermediates. As we know from the literature [6,8], the absorption spectrum of naphthalene (I) in the ultraviolet (Table 1) consists of three absorption regions. Region I is simple, having one maximum,** of high intensity. Region II possesses a fine structure, with its Maximum II in the longwave region. Region III likewise exhibits fine-structure absorption; the Maximum III of this band has very low intensity and a very narrow absorption band.*** In comparison to naphthalene, the position of Maximum I exhibits hardly any shift in the absorption spectra of 1-naphthalenesulfo acid (II), 1-naphthol [9], and 1-naphthylamine (IV) [10] (Fig. 1 and Table 1) [only in the compound (II) is it split into

* In the last stages of purification of some azo dye derivatives of the sulfo acids of 1,5-aminonaphthol that did not have sharp melting points, we determined the position of their longwave maxima, the constancy of these locations serving as an indication of the purity of the dye. The same purification method was then used for the other dyes.

** In aqueous solutions of some compounds (III, V), we observed a change in the shape of the curve taking place in the 270-330 mμ region during the measurements themselves; this change, which was manifested as a redistribution of intensity among the several bands (and their components) made it difficult to get an accurate determination of ε. The values of ε cited in this paper are therefore merely rough approximations.

*** In numbering the maxima we shall henceforth number them in the order of increasing wavelength. The one with the shortest wavelength will be Maximum I, the next one Maximum II, etc. The letters ε_1, ε_{II}... are used to denote the intensity of the respective maxima. Strictly speaking, the intensity is determined by the area of the integral $\int \varepsilon d\left(\frac{1}{\lambda}\right)$, but ε (the molar extinction coefficient) may be taken as approximately equivalent to the intensity. The wavelengths are given in mμ.

**** See following page.

TABLE 1

No.	Substance	Maxima I λ	Maxima I ε	Maxima II λ	Maxima II ε	Maxima III λ	Maxima III ε
1	Naphthalene (I)	220	10^4	275	$5.7 \cdot 10^3$	319.3	12.4
2	1-Naphthalenesulfo Acid (II)....	222 / 228	$4.9 \cdot 10^4$	275	$9.5 \cdot 10^3$	320	$2.1 \cdot 10^3$
3	1-Naphthol (III).....	229	$2.8 \cdot 10^4$	296	$4.5 \cdot 10^3$	323	$2.5 \cdot 10^3$
4	1-Naphthylamine (IV)	236	$6 \cdot 10^4$	303	$3.3 \cdot 10^3$	325	$2.7 \cdot 10^3$

2 adjacent maxima). The position of Maximum II in the spectrum of 1-naphthalene sulfo acid does not change, while it is shifted somewhat toward the visible region in the cases of 1-naphthol and 1-naphthylamine. The position of Maximum III remains the same in all three cases. The spectra of 1,5-aminonaphthol (V) (Fig. 2, Table 2) and of each of its sulfo acids – the 2-, 4-, 6-, 7-, and 8-sulfo acids (VI-X) (Fig. 3 and Table 2) exhibit 2 maxima, Maximum I being shifted slightly toward the visible region, and Maximum II being shifted somewhat more toward the longer wavelengths; Maximum III was not detected owing to the fusion of the II and III absorption bands. In the absorption spectra of the substances tested, therefore, the position of the maximum at the shortest wavelength, Maximum I, remains approximately unchanged; Maximum II is shifted toward the longer

TABLE 2

No.	Substance	Maxima I λ	Maxima I ε	Maxima II λ	Maxima II ε
1	1,5-Aminonaphthol (V)	227	$1.1 \cdot 10^5$	315	$1.9 \cdot 10^4$
2	1,5-Aminonaphthol-2-sulfo acid (VI)	233	$3.7 \cdot 10^4$	340	$8.4 \cdot 10^3$
3	1,5-Aminonaphthol-4-sulfo acid (VII)	233	$2.5 \cdot 10^4$	330	$6.5 \cdot 10^3$
4	1,5-Aminonaphthol-6-sulfo acid (VIII)	232	$1.6 \cdot 10^4$	340	$1.6 \cdot 10^4$
5	1,5-Aminonaphthol-7-sulfo acid (IX)	232	$8.2 \cdot 10^4$	325 / 342	$1.8 \cdot 10^4$ / $1.4 \cdot 10^4$

wave lengths in the following order, compared to naphthalene: 1-naphthol, 1-naphthylamine, 1,5-aminonaphthol, and the sulfo acids of 1,5-aminonaphthol; and Maximum III, which is present in the absorption spectra of Compounds (I), (II), (III), and (IV), is not displaced, while it is not visible in the spectra of 1,5 aminonaphthol and the latter's sulfo acids. In every instance the intensity of Maximum I is extremely high, while it is much lower in the second maxima, and still lower in the third. Hence, the absorption spectra of the substances tested have many features in common and retain the general nature of absorption of the naphthalene molecule.

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**** The center of gravity of a complex maximum can be determined with sufficient accuracy for Group II, but it is extraordinarily difficult for Group III, as this band is much weaker than Group II and, in some compounds (1-naphthylamine), adjoins II, so that it cannot be separated from Group II at times (1,5-aminonaphthol and its sulfo acids), even when a spectrograph of high resolving power is employed. We have therefore indicated the wavelength of the constituent group with the longest wavelength in Group III, provided the group is sufficiently isolated (319.3 in the case of naphthalene, for example).

b) Azo dyes. The absorption spectra of 1-benzeneazonaphthalene (XI) (Fig. 4, Table 3) and of the dye derived from 1-naphthylamine (XII) (Fig. 5 and Table 3) retain both of the maxima characteristic of the naphthalene molecule in the shortwave region. In the visible region, each of these spectra exhibits an entirely new longwave maximum that is lacking in naphthalene and in all of its derivatives considered hitherto, this maximum being farther toward the longer wavelengths in the spectrum of the dye (XII) than in that of the dye (XI). Salt formation, which results in the formation of dye anions, has no substantial effect upon the shortwave portion of the spectrum of either dye.

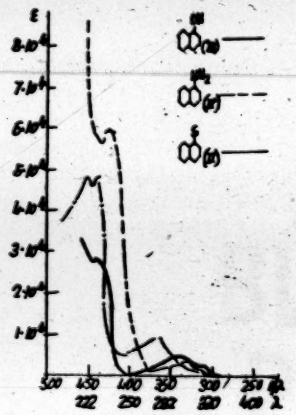


Fig. 1.

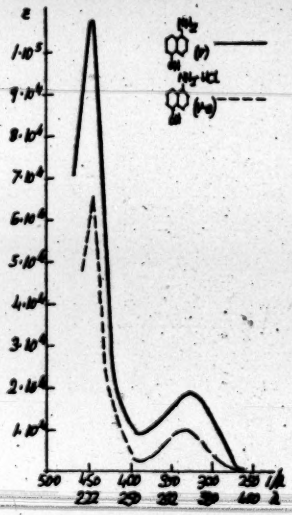


Fig. 2.

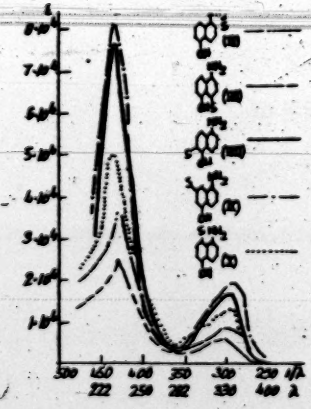


Fig. 3.

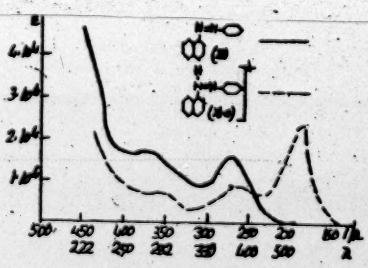


Fig. 4.

TABLE 3

No.	Substance	Maxima							
		I		II		III		IV	
		λ	ε	λ	ε	λ	ε	λ	ε
1	1-Benzeneazonaphthalene (XI)..	<223	>4.6·10⁴	270	1.7·10⁴	370	1.6·10⁴	–	–
2	1-Benzeneazonaphthalene hydrochloride (XIa)....	<230	>2.4·10⁴	280	7.4·10³	380	8.5·10³	540	2.4·10⁴
3	4-Benzeneazo-1-naphthylamine (XII).....	<223	>2.8·10⁴	250 280	2.5·10⁴ 2.5·10⁴	–	–	435	2.4·10⁴
4	4-Benzeneazo-1-naphthylamine hydrochloride (XIIa).....	<223	>2.8·10⁴	250 270	2.4·10⁴ 2.3·10⁴	300 300	1.8·10⁴ 1.5·10⁴	530	5.5·10⁴

The longwave maximum (380 mμ) of the neutral molecule is retained in the visible region of the spectrum of the cation (XI), while a new maximum much farther toward the longer wavelengths makes its appearance. An intermediate maximum (350 mμ) emerges at the boundary of the visible region in the spectrum of the cation (XII), while the longwave maximum is shifted toward the longer wavelengths. The presence of a maxima at a position close to that of the longwave maximum of 1-benzeneazonaphthalene (370 mμ) in the spectra of both dyes is worthy of note. The spectra of the dyes derived from 1-naphthol* – the dyes (XIII) and (XIV) (Fig. 6 and Table 4) – and from 1,5-aminonaphthol – the dyes (XV) and

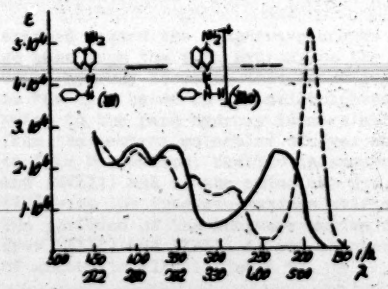


Fig. 5.

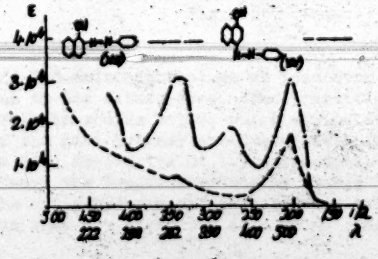


Fig. 6.

(XVI) (Fig. 7 and Table 4) – have spectra whose shortwave regions resemble those of the spectra of 1-naphthol, 1-naphthylamine, or 1,5-aminonaphthol. The spectra of some dyes contain an intermediate maximum that lies close to the longwave maximum of 1-benzeneazonaphthalene. The longwave maximum of the spectra of dyes synthesized from 1-naphthol is

*Whenever the medium is not specified, the azo dyes that contain a hydroxyl group were tested with equimolecular quantities of sodium hydroxide.

TABLE 4

No.	Substance	Maxima							
		I		II		III		IV	
		λ	ε	λ	ε	λ	ε	λ	ε
1	2-Benzeneazo-1-naphthol (XIII).....	335	$2.7\cdot10^4$	295	$3\cdot10^4$	365	$2\cdot10^4$	490	$2.3\cdot10^4$
2	4-Benzeneazo-1-naphthol (XIV).....	<208	>$2.8\cdot10^4$	290	$7\cdot10^3$	–	–	490	$1.6\cdot10^4$
3	2-Benzeneazo-1,5-aminonaphthol (XV)...	230	$2.8\cdot10^4$	300	$2.4\cdot10^4$	–	–	505	$1.1\cdot10^4$
4	8-Benzeneazo-1,5-aminonaphthol (XVI)..	<208	>$2.5\cdot10^4$	295	$7.7\cdot10^3$	350	$5.4\cdot10^3$	530	$1.2\cdot10^4$

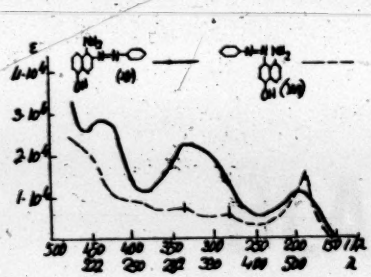


Fig. 7

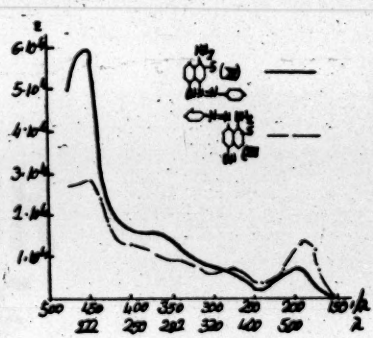


Fig. 8.

shifted toward the longerwavelengths as we pass from the para hydroxy to the ortho hydroxy isomers, this occurring in the dyes based on 1,5-aminonaphthol and 2,8-aminonaphthol as we pass from the amino to the para hydroxy isomers and even to the disazo dyes. The transition from the neutral molecules of dyes and of their sodium salts, which dissociate to form dye anions, results in spectra of the para hydroxy azo dyes (XIV), (XVI), and (XVIII) and of the amino azo dye that is a derivative of 1,5-aminonaphthol (XV) with the longwave maximum shifted toward the longer wavelengths (Table 5). The position of the longwave maxima of the ortho hydroxy and peri hydroxy azo dyes (XIII) and (XVII) is not changed when they are dissolved in a molar quantity of alcoholic alkali (Table 5).

The sulfo acids of 1,5-aminonaphthol yield azo dyes whose spectra repeat the picture already seen in the spectra of the dyes that are derivatives of 1,5-aminonaphthol (Figs. 8-12 and Tables 6-7).

Nearly all the spectra of these dyes retain both of the shortwave maxima found in the spectra of naphthalene and its intermediates: the position of Maximum I, with the shortest wavelength, is shifted negligibly, the Maximum II being shifted somewhat more. In dyes in which the sulfo group of the original sulfo acids are in the ortho position to the hydroxyl or amino group, the position of this maximum is quite close to that of the corresponding maximum in the spectrum of 1-naphthol, whereas in dyes that are derivatives of the other sulfo

TABLE 5

No.	Dye	Medium: Ethyl alcohol, λ	Medium: NaOH + ethyl alcohol, λ
1	2-(Orthohydroxy)-benzeneazo-1-naphthol (XIII)	490	490
2	4-(Parahydroxy)-benzeneazo-1-naphthol (XIV)	470	520
3	2-(Orthoamino)-benzeneazo-1,5-aminonaphthol (XV)	480	505
4	8-(Parahydroxy)-benzeneazo-1,5-aminonaphthol (XVI)	510	530
5	1-(Peri-hydroxy) benzeneazo-2,8-aminonaphthol (XVII)	500	500
6	5-(Parahydroxy)-benzeneazo-2,8, aminonaphthol (XVIII)	505	520
7	1-5-Disbenzene-azo-2,8-amino-naphthol (XIX)	530	540

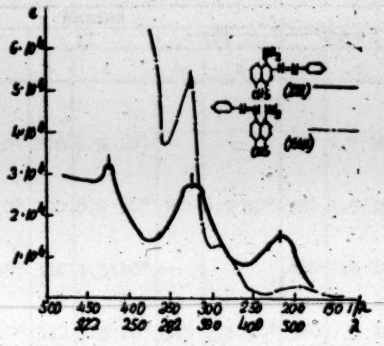


Fig. 9.

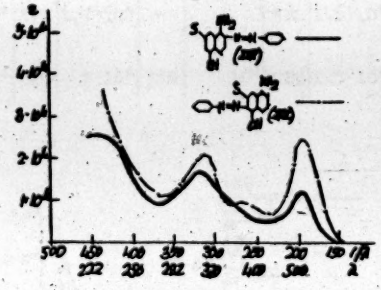


Fig. 10

acids this ... minimum is close to the longwave maximum of the spectrum of 1,5-aminonaphthol. Moreover, the spectra of all azo dyes have a longwave maximum in the visible region, its wavelength increasing as we pass from the amino to the hydroxy isomers (only in the dyes derived from 1,5-aminonaphthol-8-sulfo acid is the inverse order manifested). Lastly, the spectra of all the hydroxy azo dyes and of some of the amino azo dyes clearly exhibit a maximum whose position is close to the longwave maximum of the spectrum of 1-benzeneazonaphthalene (this maximum is not found in the spectra of dyes based on 1,5-aminonaphthol-8-sulfo ... acid). The disazo dyes that are derivatives of the 6- and 8-sulfo acids of 1,5-aminonaphthol substantially repeat the spectra of the initial monoamino azo dyes, with the exception that the introduction of another azo group shifts the longwave maximum toward the longer wavelengths.

It is appropriate to note some general pattern of behavior that may be deduced from an inspection of the spectra of the compounds tested: 1) Intermediates and azo dyes retain in their spectra the shortwave maxima that are characteristic of the naphthalene molecule, the position of the shortwave Maximum I remaining practically unchanged, and Maximum II shifting toward the visible region as we pass from naphthalene to 1-naphthol, 1-naphthylamine, 1,5-aminonaphthol, and the sulfo acids of the latter, in that order. In the azo dyes

TABLE 6

No.	Substance	Maxima I λ	I ε	II λ	II ε	III λ	III ε	IV λ	IV ε
1	4-Benzeneazo-1,5-aminonaphtholsulfo acid (XX)	220	$6.1\cdot10^4$	270	$1.5\cdot10^4$	–	–	500	$6.7\cdot10^3$
2	8-Benzeneazo-1,5-aminonaphthol-2-sulfo acid (XXI)	220	$2.8\cdot10^4$	290	$8.9\cdot10^3$	360	$6.5\cdot10^3$	520	$1.3\cdot10^4$
3	2-Benzeneazo-1,5-aminonaphthol-4-sulfo acid (XXII)	235	$3.1\cdot10^4$	310	$1.3\cdot10^4$	–	–	460	$1.6\cdot10^4$
4	8-Benzeneazo-1,5-aminonaphthol-4-sulfo acid (XXIII)	<255	>$6.5\cdot10^4$	310	$5.3\cdot10^4$	345	$1.3\cdot10^4$	520	$3\cdot10^3$
5	2-Benzeneazo-1,5-aminonaphthol-7-sulfo acid (XXIV)	230	$2.5\cdot10^4$	310	$1.7\cdot10^4$	–	–	510	$1.6\cdot10^4$
6	6-Benzeneazo-1,5-aminonaphthol-7-sulfo acid (XXV)	<227	>$2.6\cdot10^4$	320	$2\cdot10^4$	370	10^4	515	$2.5\cdot10^4$

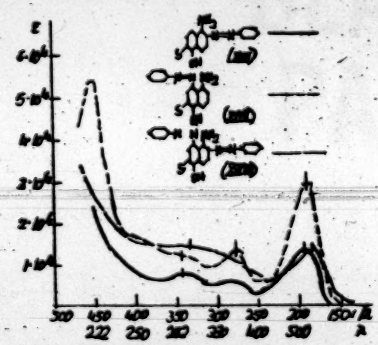


Fig. 11.

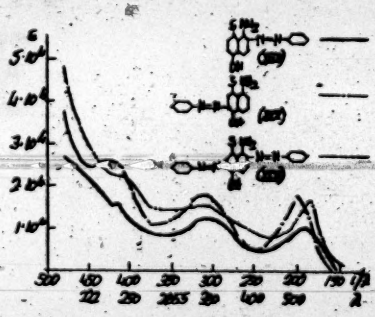


Fig. 12.

this maximum is displaced in about the same sequence. 2) Maximum III is very weak in the spectra of naphthalene, 1-naphthol, and 1-naphthylamine; it overlaps the absorption band II in the spectra of the other compounds. 3) All azo dyes possess a maximum in the visible region that is absent in the intermediates. In neutral molecules the wavelength of this maximum increases as we pass from benzeneazonaphthalene via the amino azo dyes and the para hydroxy isomers to the ortho hydroxy azo dyes, the ortho and para isomers interchanging their places in this sequence in the naphtholates. 4) Intermediate maxima appear in the spectra of some azo dyes. Most of the ortho hydroxy and para hydroxy azo dyes, for example, have a maximum that lies close to the longwave maximum of

TABLE 7

No.	Substance	Maxima							
		I		II		III		IV	
		λ	ε	λ	ε	λ	ε	λ	ε
1	2-Benzeneazo-1,5-aminonaphthol-6-sulfo acid (XXVI)....	219	$2.5 \cdot 10^4$	290	$8 \cdot 10^3$	360	$6.2 \cdot 10^3$	520	$1.4 \cdot 10^4$
2	8-Benzeneazo-1,5-aminonaphthol-6-sulfo acid (XXVII)...	222	$5.5 \cdot 10^4$	290	$1.3 \cdot 10^4$	360	$1.4 \cdot 10^3$	530	$3 \cdot 10^4$
3	2,8-Disbenzeneazo-1,5-aminonaphthol-6-sulfo acid (XXVIII)..	<215	>$3.3 \cdot 10^4$	300	$1.5 \cdot 10^4$	360	$1.4 \cdot 10^3$	540	$1.4 \cdot 10^4$
4	2-Benzeneazo-1,5-aminonaphthol-8-sulfo acid (XXIX)....	208	$2.7 \cdot 10^4$	325	$1.3 \cdot 10^4$	–	–	520	$1.2 \cdot 10^4$
5	6-Benzeneazo-1,5-aminonaphthol-8-sulfo acid (XXX)	234	$2.7 \cdot 10^4$	320	$2 \cdot 10^4$	–	–	500	$1.8 \cdot 10^4$
6	2,6-Disbenzeneazo-1,5-aminonaphthol-8-sulfo acid (XXXI	240	$2.5 \cdot 10^4$	325	$1.5 \cdot 10^4$	–	–	540	$1.7 \cdot 10^4$

the simplest naphthalene azo dye – 1-benzeneazonaphthalene. 5) Converting neutral molecules into hydrochlorides or sodium salts shifts the longwave maxima to the longer wavelengths in the spectrum. 6) Varying the pH of the medium has no effect upon the position of the longwave maxima of ortho hydroxy and peri hydroxy azo dyes. The same patterns of behavior may be observed in the absorption spectra of some other aromatic compounds: anthracene and its derivatives [12], phenylmethylpyrazolone and various dyes derived from it, and some di- and triphenylmethane dyes [13].

Thus, in addition to the well-known regularity with which the absorption spectra change as we pass from the original aromatic and heterocyclic compounds to the intermediates and dyes derived from them, we have been able to observe the reproducibility of the spectra of the parent substances in the spectra of the more complex compounds: with some deviations, the absorption spectra of intermediates and dyes reproduce the maxima (strictly speaking, the absorption bands) of the original substances. Moreover, the spectra of the dyes exhibit new maxima that are their own specific characteristics.

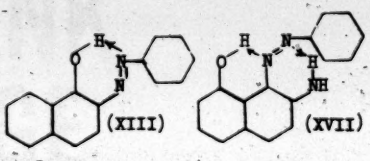
3. Evaluation of Research Results

We also endeavored to establish at least a qualitative relationship between the existence of the several maxima in the absorption spectra and the structure of the compounds under study. As we know, the wavelength of the maximum in an absorption spectrum of any molecule depends upon the excitation energy, which is given by the difference between the energies of the stationary and the excited states, these latter being governed by the differing electronic state of the molecule. It may be assumed that the Maximum I in the naphthalene spectrum (which is farthest toward the shorter wavelengths, is found in nearly all the intermediates and dyes we have tested, and has a substantial excitation energy), owes its origin largely to a change in the electronic state of the naphthalene (and only the naphthalene) ring in the molecules of these compounds. Maximum II in the naphthalene absorption spectrum lies at longer wavelengths than Maximum I, and hence has a lower excitation energy. The displacement of Maximum II in the spectra of intermediates cannot be attributed to the additive action of

the substituents, since the absorption spectra of the simplest compounds that contain the given substituent (CH_3OH and CH_3NH_2, for example [14]) possess negligible intensity, with no maxima present at all above 220 mμ. Maximum II persists in the azo dyes, also displaced toward the longer wavelengths, though less markedly so, the amount depending upon the nature of the azo constituent.

It follows from the foregoing that the origin of this maximum is due chiefly to a change in the electronic state of the naphthalene ring, as modified by the action of the substituents of the azo constituents. The longwave maximum in the absorption spectra of all azo dyes, which is absent in the naphthalene molecule and the intermediates, cannot be attributed to the azo group itself, since the absorption spectrum of the simplest compound containing an azo group – azomethane, $CH_3-N=N-CH_3$ [15] – has a spectrum whose overall intensity (including that of its maximum) is extremely low ($\varepsilon = 10$), even though it has a maximum at $\lambda = 330$ mμ, while the corresponding maximum of the absorption spectrum of 1-benzeneazonaphthalene has a $\varepsilon = 16{,}400$. Hence, the interaction of the azo group with the naphthalene ring and the substituents present in the molecule is responsible for the appearance of the longwave maximum in azo dyes. The spectra of some azo dyes exhibit other maxima in the ultraviolet and close to the visible region; it is difficult to explain their origin at the present time.

It was stated above that the position of the longwave maxima of the absorption spectra of ortho hydroxy and peri hydroxy azo dyes, (XIII) and (XVII), respectively, did not change when measurements weremade in neutral and in alkaline media. At the same time, the ortho hydroxy azo dyes were not titrated when they were tested by the potentiometric titration method [16]. Hence, the hydroxyl group did not form a naphtholate in either case. This property of ortho hydroxy and peri hydroxy azo dyes led us to assume the formation of a hydrogen bond between the hydroxyl hydrogen and the nitrogen of the azo group [11,17].



(XIII) (XVII)

SUMMARY

1. It has been established that the absorption spectra of the tested naphthalene intermediates and azo dyes repeat, with some deviations, the absorption bands (the maxima) of the spectrum of the naphthalene molecule, new and specific maxima appearing in the visible region of the spectra of the azo dyes.

2. The specific properties of ortho and peri hydroxy azo dyes may be explained by the formation of an intramolecular hydrogen bond.

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RESEARCHES ON CYANIN DYES

IV. SOME 6,6'-DIACYLAMINOTHIACARBOCYANINS

I. I. Levkoev, S. A. Kheifets, and N. S. Darvin

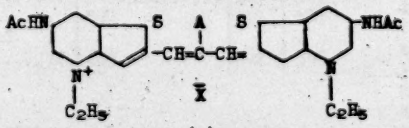
In the course of our researches on the relationship between the optical and photographic properties of cyanin dyes and their structure [1] we grew interested in the problem of the effect of the entrance of acylamino and amino groups into the heterocyclic residues of such dyes.

F. M. Hamer [2] has made a study of this problem in the quinoiso- and 2,2'-quinocarbocyanins. These researches did not enable him to arrive at any general conclusions concerning the extent of the bathochromic shift of the absorption maximum due to the entrance of an acylamino group in the heterocyclic residue of these dyes (the shift totaling 4 to 20 mμ). Nor was the question of the effect upon the color of dyes produced by acylating the amino groups present in their heterocyclic residues (the effect being hypsochromic in some cases and bathochromic in others).

A. P. Kiprianov has synthesized thiacarbocyanins containing methyl, carbamino, benzoylamino, and p-tolusulfamino groups in the 6,6'-positions, as well as 8,10-diacetaminothiacarbocyanine [3]. The literature also contains data on the optical properties of some 6,6'-diacetaminothiacarbocyanins [3-6,14].

This research has shown that in the transition from 6,6'-diaminothiacarbocyanins to the corresponding acylamino derivatives, as well as in the 6,6'-diamino-2,2'-quinocarbocyanins [2], the absorption maximum of the dyes is shifted substantially toward the shorter wavelengths. This hypsochromic effect is apparently due to the fact that fewer electrons are diverted from the nitrogen atoms to the polymethyne chromophore when the amino groups are acetylated [3-7]. On the other hand, 6,6'-bis-(dimethylamino)-7,7'-diacetaminothiacarbocyanins have a deeper color than the corresponding 6,6'-bis-(dimethylamino)-7,7'-diamino derivatives [8], which it is interesting to contrast with the properties of 5- and 7'-amino- and 5- and 7'-acylaminoquinoisocyanins [2].

In the present research we have synthesized several 6,6'-di-(formylamino)-6,6'-diacetamino)- and 6,6'-di-(methylsulfamino)-thiacarbocyanins (I) and investigated the optical and photographic properties of these dyes.



(I)

Ac = CHO-, CH_3CO, or CH_3SO_2; A = H, CH_3, or C_2H_5;
X = acid residue

We synthesized the original 6-formylamino- and 6-methylsulfamino-2-methylbenzothiazoles, as well as the 6-acetamino-2-methylbenzothiazole briefly described previously [9], by acylating 6-amino-2-methylbenzothiazole [9,10].

Heating 6-amino-2-methylbenzothiazole with an excess of formic acid yielded the formate 6-formylamino-2-methylbenzothiazole, which was stable in water and was converted into a base by treatment with bicarbonate.

No acetate was formed from 6-acetamino-2-methylbenzothiazole under similar conditions. The reaction of 6-acetamino- and 6-methylsulfamino-2-methylbenzothiazoles with p-toluene sulfonates yielded quaternary salts of these bases. Heating them with ortho esters of carboxylic acids in pyridine [11] yielded the respective carbocyanins, which were recovered as bromides or iodides.

Dicarbo- and 4'-cyanin, as well as the 2-p-dimethylaminostyryl derivative, were synthesized from the ethyl-p-toluene sulfonate of 2-methyl-6-acetaminobenzothiazole in the usual manner.

Heating 6-formylamino-2 methylbenzothiazole to 120° with the ethyl ester of p-toluenesulfonic acid apparently causes a partial ethylation of the formylamino group, so that we were unable to secure the quaternary salt in the pure state. We were able to secure a methiodide by heating 6-formylamino-2-methylbenzothiazole to 70° with an excess of methyl iodide, while formylation of the quaternary salts of 5 amino-2-methylbenzothiazole yielded the corresponding ethobromide and ethiodide. We found, however, that these salts condense with difficulty with ortho esters of carboxylic acids in pyridine to yield carbocyanines.

In this connection we synthesized 6,6'-di-(formylamino)-thiacarbocyanins by formylating 6,6'-diamino derivatives, the latter being prepared by heating 6,6'-di-(acetamino)-thiacarbocyanins with 25% hydrochloric acid.

The absorption maxima of the synthesized ethoxides of 6,6'-di-(acylamino)-thiacarbocyanins (in ethyl alcohol) are listed in Table 1.

TABLE 1

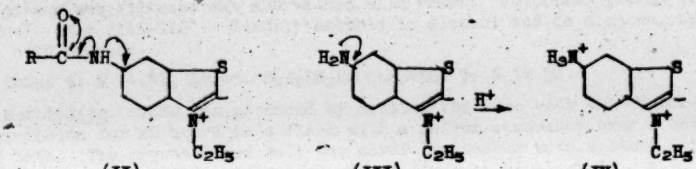
Positions of the Absorption Maxima of 3,3'-Diethyl-6,6'-di-(acylamino)-thiacarbocyanins in Ethyl Alcohol

Substituents at the 6,6' positions	Position of the absorption maxima, mμ		
	Substituents at the 9 position		
	H	CH_3	C_2H_5
H	557	543	547
NH_2	594 (596) [3,8]	583	587
CHONH	575	561	565
CH_3CONH	577 (581) [3,8]	563	567
CH_3SO_2NH	572	559	563
CH_3SO_2NH (+ 30 mol. NaOH).....	605	592	596

As we see in Table 1, acylating the amino groups of 6,6'-diaminothiacarbocyanins that have no substituents attached to the chain displaces the absorption maximum of the dyes 17-22 mμ toward the shorter wavelengths of the spectrum in the cases tested. Comparison of the absorption maxima of 6,6'-di-(methylcarbamino)-[3], 6,6'-di-(acetamino)-, and 6,6'-di-(formylamino)-thiacarbocyanins indicates that this hypsochromic shift increases with the nature of the acyl group in the following order: $COOCH_3 < COCH_3 < COH$. (The absorption maxima of ethoxides of dyes without substituents in the chain are 579, 577, and 575 mμ, respectively.

This is apparently related to the successive increases in the diverting of

electrons from the nitrogen atom to the carbonyl oxygen in the respective dyes, which naturally results in a diminution of the electron shifts from the nitrogen to the polymethyne chain (II).



(II) (III) (IV)

As A.I.Kiprianov has noted [6], the deepening in the color of thiacarbocyanins when electron donor groups enter their heterocyclic residues is related to electron shifts from these substituents to the polymethyne chromophore. The increase in color intensity in the transition from the 6,6'-diaminothiacarbocyanins (III) to the salts (IV), in which this displacement does not occur, is confirmation of this assertion. The absorption maxima of these salts coincide nearly completely with those of thiacarbocyanins that have unsubstituted heterocyclic residues [7].

The higher color observed in the transition from the 6,6'-diamino- to the 6,6'-di-(methylsulfamino)-thiacarbocyanins is likewise due, apparently, to a decrease in the electron displacements from the substituent groups to the polymethyne chromophore [3,6].

There are no references in the literature to the photographic properties of di(acylamino)-thiacarbocyanins. Some thia- and selenacyanins containing acylamino groups have been proposed, however, as sensitizers for silver halide emulsions [12].

Photographic investigations of 6,6'-di-(formylamino)- and 6,6'-di-(acetamino)-thiacarbocyanins has indicated that many of them are not inferior to the corresponding dyes without substituents in the heterocyclic residues as sensitizers, and even surpass them in some cases; the 6,6'-bis-(methylsulfamino) derivatives are somewhat less effective. Under ordinary conditions the dyes of this group do not yield sensitizers of the second order [13].

In contrast to the 6,6'-diaminothiacarbocyanins, dyes that contain acylamino groups do not exhibit fogging or desensitizing action.

EXPERIMENTAL

(In association with V.V.Daruashkina)

6-Formylamino-2-methylbenzothiazole

8.2 g of 6-amino-2-methylbenzothiazole (m.p. 120-121°) was heated with 11.2 g of anhydrous formic acid for 3 hours in a flask with a reflux condenser over an oil bath to an oil temperature of 120-130°. After the solution had cooled, 100 ml of anhydrous benzene was added, a slightly yellowish crystalline precipitate of the formate settling out, which was filtered out and washed with benzene. The yield was 11.25 g (96% of the theoretical). M.p. 95-97°. Slightly yellowish needles (from water); readily soluble in ethyl alcohol, only slightly soluble in water.

Found %: N 11.75; 11.87. $C_9H_8ON_2S \cdot CH_2O_2$. Computed %: N 11.76.

In order to recover the base, the formate was dissolved in ethyl alcohol (5.8 g in 20 ml), an aqueous solution of sodium bicarbonate was added (3.36 g in 40 ml), and the mixture was diluted with 60 ml of water. The resultant precipitate was filtered out and washed with water. Colorless prisms (from benzene). M.p. 111-112°. Readily soluble in alcohol and in acetone, sparingly so in cold benzene.

Found %: N 14.41, 14.45. $C_8H_8ON_2S$. Computed %: N 14.58.

Methiodide. This was produced by heating the base with a 100% excess of methyl iodide for 20 hours in a flask with a reflux condenser over a boiling water bath. The crystallized salt was carefully washed with acetone. Yield: 50.9% of the theoretical. Colorless prisms (from ethyl alcohol). M.p. 252-253°.

Found %: N 8.39, 8.52. $C_{10}H_{11}ON_2SI$. Computed %: N 8.38.

Methobromide. 1.0 g of 2-methyl-6-aminobenzothiazole methobromide was boiled for 3 hours with 2 ml of formic acid in a flask fitted with a reflux condenser. The mixture was diluted with ether, and the precipitate was filtered out and washed with acetone. The yield was 87% of the theoretical. Colorless needles (from ethyl alcohol). M.p. 238-239°. A sample of the salt fused at 223-236° when mixed with 2-methyl-6-aminobenzothiazole methobromide.

Found %: N 9.23, 9.24. $C_{11}H_{13}ON_2SBr$. Computed %: N 9.30.

Ethiodide. This was prepared from 2-methyl-6-aminobenzothiazole ethiodide, analogously to the preceding compound. The reaction mixture was diluted with a 10% solution of potassium iodide, and the precipitate was filtered out and washed with water. The yield was 81% of the theoretical. Heating equimolar quantities of 6-formylamino-2-methylbenzothiazole and ethyl iodide for 20 hours over a boiling water bath in a flask fitted with a reflux condenser resulted in a yield of the ethiodide that was 22% of the theoretical. Colorless needles (from ethyl alcohol). M.p. 243-244°.

Found %: N 8.01, 7.90. $C_{11}H_{13}ON_2SI$. Computed %: N 8.04.

6-Acetoamino-2-methylbenzothiazole

16.8 g of acetic anhydride was gradually added to 180.4 g of 6-amino-2-methylbenzothiazole dissolved in 65 ml of benzene, and the mixture was heated for 30 minutes over a boiling water bath in a flask fitted with a reflux condenser. After the contents had cooled, the precipitate was filtered out and washed with 15 ml of benzene. The yield was 89% of the theoretical. M.p. 146-147°. The product was purified by recrystallizing it from water (1:100) and drying it at 90-100°. Colorless lustrous crystals with a m.p. of 148-149° (the m.p. is given as 149-150° by Browning et al. [9]).

Picrate: yellow prisms (from ethyl alcohol). M.p. 218-219°.

Methiodide. This was prepared by heating 0.82 g of the base for 6 hours with 0.78 g of the methylester of p-toluenesulfonic acid and then dissolving the methyl-p-tolusulfonate in 10 ml of water and adding 15 g of potassium iodide. The precipitate was washed with water and with acetone. The yield was 64% of the theoretical. Colorless needles (from methanol); m.p. 252-254°.

Found %: I 36.32. $C_{11}H_{13}ON_2SI$. Computed %: I 36.46.

Ethyl-p-toluenesulfonate. A mixture of 0.41 g of the base and 0.42 g of the ethyl ester of p-toluenesulfonic acid was heated to 145-150° for 6 hours. The crystallized mass was washed with benzene and with acetone. The yield was 0.77 g (95% of the theoretical). M.p. 192-194°. For analysis, the salt was recrystallized from a 19:1 mixture of acetone and ethyl alcohol. Nearly colorless hygroscopic needles with a m.p. of 197°; very freely soluble in water and

* to 145-150°

alcohol; less so in acetone.

Found %: N 7.02, 6.94. $C_{18}H_{22}O_4N_2S_2$. Computed %: N 6.94.

Ethiodide. This was prepared by adding 2.0 g of potassium iodide to an aqueous solution of the preceding compound (2 g in 10 ml). Colorless needles (from ethyl alcohol). M.p. 230-232.

Found %: N 7.65. $C_{12}H_{15}ON_2SI$. Computed %: N 7.73.

Ethylperchlorate. Colorless prisms (from water). M.p. 262-263°. Rather slightly soluble in ethyl alcohol.

6-Methylsulfoamino-2-methylbenzothiazole

8.2 g 6-amino-2-methylbenzothiazole was dissolved in 25 ml of anhydrous pyridine, 6.3 g of freshly distilled methyl sulfochloride was added, and the mixture was heated for an hour over a boiling water bath. The liquid was diluted with 220 ml of 3% hydrochloric acid, and the slightly pinkish precipitate was filtered out and washed with water. The yield was 10.6 g (86% of the theoretical). M.p. 142-143°. The product was purified by recrystallizing it from water (1:550) and then from ethyl alcohol (1:20). Colorless orthogonal lamellae with a m.p. of 145-146°. Rather freely soluble in ethyl alcohol and acetone; less so in benzene.

Found %: S 26.46, 26.30. $C_9H_{10}O_2N_2S_2$. Computed %: S 26.48.

Ethiodide. A mixture of 0.48 g of the base and 0.42 g of the ethyl ester of p-toluenesulfonic acid was heated for 6 hours to 130°. The brown mass was then dissolved in 10 ml of water, the impurities were extracted with ether, and the aqueous solution was heated with activated charcoal. The solution was nearly colorless after filtration, and 2 g of potassium iodide was added to it. The precipitated ethiodide was filtered out and washed with 3 ml of water and with acetone. The yield was 71% of the theoretical. Colorless lamellae (from methanol). M.p. 247-248°.

Found %: N 6.80, 7.06. $C_{11}H_{15}O_2N_2SI$. Computed %: N 7.03.

6,6'-Di-(acetoamino)- and 6,6'-Di-(methylsulfamino)-3,3'-diethylthiacarbocyanins

The carbocyanins were prepared by heating the 6-acetamino- and 6-methylsulfamino-2-methylbenzothiazoles for 6 hours with an excess of the ethyl ester of p-toluenesulfonic acid (to 145° for the acetamino derivative and to 125-130° for the 6-methylsulfamino derivative). Ethyl orthocarbonate and pyridine were added to the quaternary salt, and the mixture was heated over an oil bath to 130° (oil temperature). Then the dye was precipitated with ether, dissolved in methanol, and recovered as the bromide by adding a 10% aqueous solution of potassium bromide. The precipitated dyes were carefully washed with alcohol, water, and ether and dried, after which they were crystallized from methanol or ethyl alcohol with a constant melting point.

Some of the dyes were also isolated as their iodides and p-tolusulfonates. All the dyes were dried at 100° to constant weight before analysis. Some of them contained crystallization alcohol.

The conditions employed in synthesizing the dyes, their properties, and the analysis results are given in Table 2.

3,3'-Diethyl-6,6'-diaminothiacarbocyanin Iodide [2]

1.0 g of 3,3'-diethyl-6,6'-di-(acetamino)-thiacarbocyanin p-tolusulfonate

TABLE 2

Name of Dye	Quantity: Base, (g)	Quantity: Ester p-toluenesulfonic acid, (g)	Ortho ester (g) ****	Heating time at 130°, min.	Quantity pyridine, ml	Crystallization solvent	Yield (% of theory)	Appearance	Melting point, (°)	Analysis: % Br found	Analysis: Formula	Analysis: % Br
3,3 -Diethyl-6,6 -di-(acetamino)-thiacarbocyanin bromide*.....	1.08	1.06	I; 1.46	30	6.5	C_2H_5OH	79	Lustrous green prisms	271-272	14.08 14.18	$C_{29}H_{27}O_2N_4S_2Br$	14.29
3,3 -Diethyl-9-methyl-6,6 -di-(acetamino)-thiacarbocyanin bromide **	0.41	0.42	II; 0.65	30	2.5	CH_3OH	56	Fine violet or blue crystals	283	13.79	$C_{30}H_{29}O_2N_4S_2Br$	13.94
3,3 ,9-Triethyl-6,6 -di-(acetamino)-thiacarbocyanin bromide ***	0.41	0.42	III; 0.70	45	2.5	C_2H_5OH	47	Orthogonal green lamellae	260-261	13.50	$C_{31}H_{31}O_2N_4S_2Br$	13.61
3,3 -Diethyl-6,6 -di-(methylsulfamino)-thiacarbocyanin bromide.....	0.48	0.42	I; 0.60	40	3	C_2H_5OH	49	Light-violet prisms	300-301	12.82	$C_{29}H_{27}O_4N_4S_4Br$	12.65
3,3 -Diethyl-9-methyl-6,6 -di-(methylsulfamino)-thiacarbocyanin bromide.....	0.48	0.42	II; 0.65	40	3	C_2H_5OH	34	Violet prisms	278-280	12.44 12.30	$C_{30}H_{29}O_4N_4S_4Br$	12.38
3,3-Triethyl-6,6-Di-(methylsulfamino)-thiacarbocyanin bromide.....	0.48	0.42	866; 0.70	55	3	CH_3OH	38	Violet prisms	250-252	12.25 12.23	$C_{31}H_{31}O_4N_4S_4Br$	12.12

* Iodide – dark-green needles (from methanol). M.P. 296-299°. p-Toluenesulfonate – lustrous green needles (from ethyl alcohol). M.P. 290-291°.

** p-Toluenesulfonate – blue-violet needles (from methanol). M.p. 281-282°. Iodide – violet prisms (from methanol). M.p. 304-306°.

*** Iodide – blue crystals (from methanol). M.p. 278°.

**** Ortho ester designations: I – ethyl orthoformate; II – ethyl orthoacetate; III – ethyl orthopropionate.

was dissolved in 35 ml of 25% hydrochloric acid, and the solution was boiled for 20 minutes in a flask fitted with a reflux condenser. The liquid was then diluted with 30 ml of water and 3 g of potassium iodide was added, after which it was chilled and aqueous ammonia was added until its reaction was slightly alkaline. The precipitated dye was filtered out, washed with 25 ml of water, dried (weight 0.65 g, 81% of the theoretical), and crystallized twice from ethyl alcohol (1:450). Lustrous dark-blue prisms with a m.p. of 232°, soluble with some difficulty in ethyl alcohol. They contain crystallization alcohol.

Found %: N 9.96, 9.80. $C_{21}H_{23}N_4S_2I \cdot C_2H_5OH$. Computed %: N 9.86.

3,3'-Diethyl-9-methyl-6,6'-diaminothiacarbocyanin Iodide

This was synthesized by boiling a solution of 1.5 g of 3,3'-diethyl-9-methyl-6,6'-di-(acetamino)-thiacarbocyanin p-tolusulfonate in 30 ml of 25% hydrochloric acid for 20 minutes, followed by the addition of potassium iodide and neutralization with ammonia. The yield was 0.94 g (61% of the theoretical).

Lustrous green prisms with a m.p. of 237-239° (from ethyl alcohol, 1:350). Soluble with some difficulty in ethyl alcohol. They contain crystallization alcohol, some of which is lost at 80° in vacuum.

Found %: N 8.94, 9.14. $C_{22}H_{25}N_4S_2I \cdot 2C_2H_5OH$. Computed %: N 8.92.

3,3'-Diethyl-6,6'-di-(formylamino)-thiacarbocyanin Iodide

0.40 g of 3,3'-diethyl-6,6'-diaminothiacarbocyanin iodide was boiled for one hour in a flask fitted with a reflux condenser with 12 ml of anhydrous formic acid. The violet-red solution was diluted with 40 ml of water, 2 g of potassium iodide was added, and the liquid was chilled and alkalinized with aqueous ammonia. The precipitated dye was filtered out and washed with water, alcohol, and ether. The yield was 0.41 g (91% of the theoretical).

The dye was purified by crystallizing it twice from methanol. Lustrous grayish-blue prisms, with a m.p. of 295-297°, slightly soluble in ethyl alcohol and containing crystallization methanol.

Found %: 9.19, 9.26. $C_{23}H_{23}O_2N_4S_2ICH_3OH$. Computed %: N 9.18.

3,3',9-Triethyl-6,6'-diaminothiacarbocyanin Iodide

This was synthesized, like the preceding dye, by boiling 1.0 g of 3,3',9-triethyl-6,6'-di-(acetamino)-thiacarbocyanin iodide with 20 ml of 25% hydrochloric acid to saponify it. The yield was 87% of the theoretical. Lustrous dark-green prisms (from ethyl alcohol, 1:240). M.p. 231-232°. They contain crystallization alcohol.

Found %: N 9.57, 9.61. $C_{23}H_{27}N_4S_2I \cdot C_2H_5OH$. Computed %: N 9.40.

3,3'-Diethyl-9-methyl-6,6'-di-(formylamino)-thiacarbocyanin Iodide

This was synthesized by boiling 0.3 g of 3,3'-diethyl-9-methyl-6,6'-diaminothiacarbocyanin iodide for 1 hour with 9 ml of formic acid, followed by dilution with water and neutralization with ammonia. The yield was 82% of the theoretical. Minute violet needles (from methanol). M.p. 231-233°. They contain crystallization methanol, only part of which is driven off at 80-100° in vacuum.

Found %: N 8.77, 8.65. $C_{24}H_{25}O_2N_4S_2I \cdot 2CH_3OH$. Computed %: N 8.53.

3,3',9-Triethyl-6,6' di-(formylamino)-thiacarbocyanin Iodide

This was synthesized, like the preceding dye, by boiling 3,3'9-triethyl-6,6'-diaminothiacarbocyanin iodide (0.40 g) with formic acid (10 ml). The yield was

95% of the theoretical. Minute bluish-violet prisms (from methanol, 1:100). M.p. 271-273°. They contain crystallization methanol.

Found %: N 8.72, 8.69. $C_{25}H_{27}O_2N_4S_2I \cdot CH_3OH$. Computed %: N 8.79.

3,3'-Diethyl-6,6'-di-(acetamino)-thiacarbocyanin p-Tolusulfonate

0.82 g of the ethyl-p-tolusulfonate of 6-acetamino-2-methylbenzothiazole and 0.27 g of the dianil hydrochloride of malonaldehyde were dissolved in 6 ml of absolute alcohol, 0.14 g of sodium dissolved in 1.5 ml of absolute ethyl alcohol was added, and the whole was boiled for 20 minutes. The resulting precipitate was filtered out and washed with water and then with alcohol until the filtrate was a pure blue. The yield was 0.24 g (35% of the theoretical). Light green needles with a golden iridescence (from methanol). M.p. 243°. Absorption maximum at 670 mμ. The dye was dried in vacuum at 90° before being analyzed.

Found %: N 8.41, 8.44. $C_{34}H_{36}O_5N_4S_3$. Computed %: N 8.28.

3,1'-Diethyl-6-acetaminothia-4'cyanin Iodide

0.82 g of the ethyl-p-tolusulfonate of 6-acetamino-2-methylbenzothiazole and 1.14 g of quinoline ethiodide were dissolved in 7 ml of absolute ethyl alcohol, a solution of 0.14 g of sodium in 3 ml of absolute ethyl alcohol was added, and the whole was boiled for 15 minutes in a flask fitted with a reflux condenser. After the mixture had cooled, the precipitated dye was filtered out and washed with water and with alcohol. The yield was 0.33 g (63% of the theoretical). Thin red needles (from methanol). M.p. 301°. Absorption maximum 512 m , (in ethyl alcohol). The dye was dried in vacuum at 100° before being analyzed.

Found %: N 8.30, 8.22. $C_{23}H_{24}ON_3SI$. Computed %: N 8.12.

Ethyl-p-tolusulfonate of 2-p-Diethylaminostyryl-6-acetaminobenzothiazole [14]

0.82 g of the ethyl-p-tolusulfonate of 6-acetamino-2-methylbenzothiazole and 0.36 g of p-dimethylaminobenzaldehyde were dissolved in 4 ml of absolute ethyl alcohol, 0.04 g of piperidine was added, and the solution was boiled for 2 hours in a flask fitted with a reflux condenser. After the contents had cooled, the dye was filtered out and washed with water and with alcohol. The yield was 0.83 g (77% of the theoretical). Red needles (from methanol). M.p. 273-274°.

The ethiodide was secured by adding a 10% aqueous solution of potassium iodide to a solution of the ethyl-p-tolusulfonate in methanol. Blue-violet needles (from methanol). M.p. 265°. Absorption maximum at 532 mμ (530) [14]. The dye was dried in vacuum at 120° before analysis.

Found %: N 8.47, 8.39. $C_{21}H_{24}ON_3SI$. Computed %: N 8.52.

SUMMARY

1. The 6-formylamino- and 6-methylsulfamino-2-methylbenzothiazoles have been synthesized, together with the quaternary salts of these bases and 6-acetamino-2-methylbenzothiazole.

2. Several thiacarbocyanins containing the formylamino, acetamino, methylsulfamino, and amino groups at the 6,6'-positions have been synthesized. The absorption spectra of alcoholic solutions of these dyes have been measured, and their photographic properties have been investigated.

3. When the amino groups of 6,6'-diaminothiacarbocyanins that are unsubsti-

tuted along the chain are acylated, the dyes' absorption maxima are displaced 15-22 mμ toward the shorter wavelengths, the amount of this displacement depending upon the nature of the acyl group.

4. Most of the 6,6'-di-(formylamino)- and 6,6'-di-(acetamino)-thiacarbocyanins are as good sensitizers as dyes that have no substituents in their heterocyclic rings. The thiacarbocyanins that contain acylamino groups do not possess much capacity for second-order sensitization.

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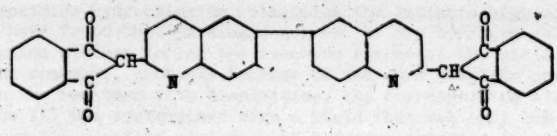
RESEARCHES ON THE DERIVATIVES OF QUINOLINE

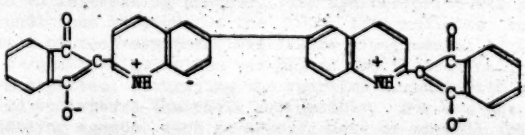
VIII. SYNTHESIS OF SUBSTANTIVE QUINOPHTHALONIC DYES FROM DIPHENYLDIAMINES *

V. I. Ardashev and Z. V. Malina

In 1937 A.E.Porai-Koshits and Kulikov [1], applying the analogy in the structure of acid and substantive azo dyes (the latter possessing a "twinned" formula), synthesized the first substantive biquinophthalonic yellow dye from biquinaldine and phthalic anhydride by "twinning" the quinophthalone molecule:



The dipole formula proposed by Kuhn for quinophthalone is in better agreement with the requirements of color theory, as it contains a rather long system of conjugated double bonds [2]:



The biquinaldine required for this synthesis was prepared by the Döbner-Miller method, using arsenic acid as the oxidizing agent; this doubled the yield, which was 17.6% of the theoretical. In contrast to benzidine azo dyes, dyes of this type do not change color when treated with acids and could be employed industrially if we only had an economically satisfactory method of securing biquinaldine products [1].

The objective of the present research has been the synthesis of biquinaldine derivatives of diphenyldiamines: benzidine, tolidine, and dianisidine, and then securing from them the respective quinophthalonic substantive dyes. An attempt to secure biquinaldine intermediates by the method we had developed for the monoamines (involving their joint condensation with ethylene glycol and acetone [3]) failed when diamines were used in the reaction, as considerable tarring occurred, while the yields of the end products were low. We then employed the Beyer reaction [4]:

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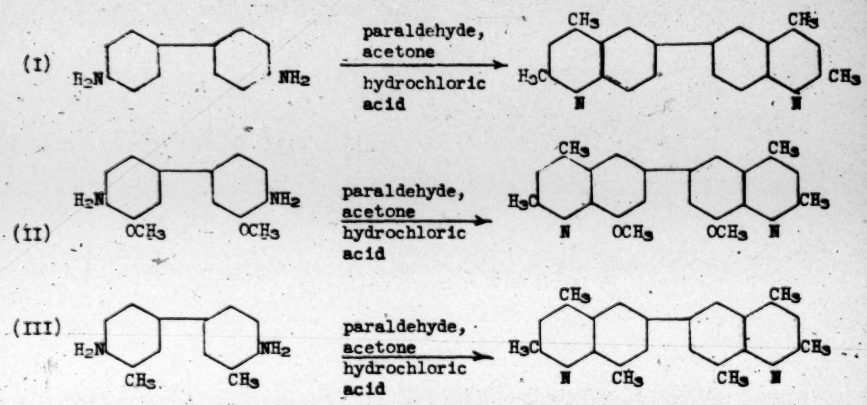
* Report VII has been published in the Scientific Papers of Rostov State University, No. 5 (1951).

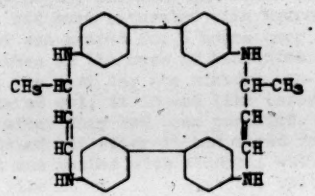


Schestopal used this method to synthesize tetramethylbiquinoline (Equation (I) from benzidine with a yield that was some 30% of the theoretical [5]; he used washing with alcohol to separate the tetramethylbiquinoline hydrochloride from the unreacted benzidine hydrochloride, utilizing the latter's high solubility in alcohol. We have found that passing a current of dry hydrogen chloride through the reaction mixture during the reaction increases the yield of the tetramethylbiquinoline somewhat, probably because of the more complete precipitation of its salt. In the reaction with dianisidine, the corresponding biquinoline product (Equation II) was synthesized with a yield that was only 18% of the theoretical, saturating the reaction mixture with hydrogen chloride failing to raise the yield, owing to the onset of tarring, which may be due to the phenolic nature of this product. The synthesis of hexamethylbiquinoline from tolidine (Equation III) was an interesting process. Its hydrochloride was not precipitated under the conditions adopted for the other intermediates, so that we resorted to the method of recovery described in the experimental section below. The yield of the hexamethylbiquinoline was 51% of the theoretical. In this case, as might have been expected, saturating the reaction mixture with gaseous hydrogen chloride failed to improve the yield perceptibly. Nor was the yield improved by the use of oxidizing agents, such as arsenic acid or stannic chloride. But when it is borne in mind that the yield of quinoline preparations in the Beyer reaction is ordinarily 30%, the use of tolidine in this reaction is worthy of note, the method we adopted also involving the regeneration of the unreacted amine. The substantive quinophthalonic dyes secured from the synthesized intermediates dyed cotton in a soda-alkali bath with Glauber salt the following colors: dark yellow with the dye based on benzidine; dark yellow with a faint tinge of orange with the dye based on tolidine; and orange with the dye based on dianisidine. In slightly acid baths silk is dyed deeper shades that are various tints of brown.

In the synthesis of quinoline derivatives from aromatic amines and propylene glycol we have already remarked that syntheses in the presence of acetone provide a higher yield [6].

The cited research on benzidine likewise demonstrates that the diamines furnish a higher yield of quinoline bases in the Beyer reaction than in the Döbner-Miller reaction. This may be due to the different mechanism involved in these reactions. In the Döbner-Miller reaction it is highly probable that

Eibner-Eckstein bases are formed, which are of cyclic structure in the case of diamines: for benzidine, for example, we have:



As the formation of a cyclic base is impeded, the reaction follows another course, resulting in a lowering of the yield of the quinoline base. It is worthy of note that the apparent object of the preliminary saturation of the acetone-paraldehyde mixture with hydrogen chloride, which is so widely practiced in the Beyer reaction, involves the maximum formation of a ketal, whose presence we do not consider essential, since we believe that the principal course followed by this reaction is the formation of ethylidene bases [3]. Indeed, in our investigation of a mixture of paraldehyde and acetone, we have found that acetone is unaffected, being merely a solvent, while the aldehyde forms the α,α'-dichloroethyl ether usually resulting under these conditions [3]. When this ether is heated with water, as is the case in the Beyer reaction, it is decomposed into acetaldehyde and hydrochloric acid:

$$(CH_3CHCl)_2O + H_2O \longrightarrow 2CH_3C\begin{matrix}O\\H\end{matrix} + 2HCl.$$

The gradual evolution of the aldehyde ensures the even course of the reaction and diminishes tarring.

EXPERIMENTAL

Synthesis of 2,2',4,4'-tetramethylbiquinoline. Experiment 1. A mixture of 30 ml of paraldehyde and 36 ml of acetone was placed in a half-liter flask and chilled with ice while a current of anhydrous hydrogen chloride was passed through until it was saturated. This took 1-1.5 hours, after which it was set aside to stand for about 24 hours. The next day the mixture was placed in a half-liter round-bottomed flask containing 12.3 g of benzidine and 30 ml of concentrated hydrochloric acid (sp. gr. 1.19), which had been thoroughly stirred together. The flask was connected to a reflux condenser, and the reaction mixture was heated over a water bath for 5 hours, after which it was allowed to stand overnight. The next day the crystallized mass was boiled, 50 ml of water being added, and then the tar was filtered out of the hot solution. As the filtrate cooled, the hydrochlorides of the bases settled; they were filtered out and washed on the filtrate with alcohol. This caused the benzidine hydrochloride to dissolve in the alcohol, while the tetramethylbiquinoline salt remained on the filter. Decomposing the latter with a 40% solution of sodium hydroxide yielded the free base, with a m.p. of 224°, the melting point rising to a constant 232° after recrystallization from alcohol. The yield of the base was 5.41 g, or 26% of the theoretical.

Experiment 2. A current of anhydrous hydrogen chloride was passed through the reaction mixture while it was heated over the water bath. The resultant product was much purer. The melting point of the base precipitated from its salt was 228°. The yield was 6.5 g, or 31.2% of the theoretical.

Synthesis of 2,2',4,4'-tetramethyl-8,8'-dimethoxybiquinoline. Experiment 3. 16.3 g of dianisidine and 30 ml of hydrochloric acid were placed in a half-liter flask; the mixture was thoroughly stirred, and a mixture of 30 ml of paraldehyde and 36 ml of acetone that had been saturated with hydrogen chloride the day before was added. The flask was heated for 5 hours over a water bath, the reaction being much more vigorous than in the case of benzidine. Then the flask was allowed to stand overnight; the next day the mixture was decomposed with water and boiled. The tar was filtered out; it looked like tarry crystals, which proved to be unreacted dianisidine after they had been purified. The filtrate was cooled, and the hydrochloride settled out after it had stood for two or three hours. The dianisidine hydrochloride was washed with alcohol, while the salt of the biquinoline base, which looked like [illegible] lustrous white leaflets, was decomposed with alkali. The yield of the crude base was 4.4 g, or 18% of the theoretical. Its melting point was not sharp, the substance turning into a thick mass that did not flow along the walls of the capillary at 115° and finally melting at 180°. It was recrystallized twice from alcohol, yielding a constant m.p. of 195°.

Synthesis of 2,2',4,4',8,8'-hexamethylbiquinoline. Experiment 4. 14.2 g of tolidine was placed in a half-liter flask and thoroughly mixed with 30 ml of concentrated hydrochloric acid, after which a mixture of 35 ml of paraldehyde and 40 ml of acetone that had been saturated with hydrogen chloride the day before was added, and the flask was heated for 5 hours over a water bath. The next day the reaction mixture was diluted with 50 ml of water and cautiously boiled, because a dense precipitate that was only sparingly soluble in a hydrochloric-acid medium formed at the bottom of the flask; it was filtered out together with the tar. This tarry precipitate was boiled in water that had been acidulated with hydrochloric acid, after which the tar was filtered out. The pure hexamethylbiquinoline base was precipitated from the filtrate by a sodium hydroxide solution as 0.9 g of a white powder with a m.p. of 225°, yield being 4% of the theoretical. Recrystallization from alcohol did not affect its melting point. In contrast to the experiments with benzidine and dianisidine, no hydrochlorides settled out of the first filtrate. We then precipitated the base with a 30% solution of sodium hydroxide after having diluted the mixture considerably with water. This threw down 17.7 g of a crystalline precipitate with a m.p. of 176-180°. The use of various methods of separating and purifying the resultant mixture of bases, such as diazotization, separation by means of ferrocyanides, converting the biquinoline base into a dichromate, and the like, all failed to yield a satisfactory result. We finally hit upon treating the crude product with phthalic anhydride, as suggested by A.E.Porai-Koshits [8], involving the phthalic-anhydride processing of the quinoline derivatives mixed with the amines, both in various solvents and without any solvent. The primary amines react with the anhydride, forming arylphthalamic acids of the $C_6H_4<^{CONHR}_{COOH}$ type, where R is the respective aromatic radical. These acids can be separated from the quinoline derivatives by dissolving them in aqueous caustic alkalies or in soda. Then the alkaline solution of the arylphthalamic acid can be saponified in an autoclave to recover the phthalic acid as well as the primary amine. After testing various solvents we selected ether. The precipitated bases were treated with 25 ml of ether, the undissolved residue being filtered out and dried. This yielded 7.8 g of purified hexamethylbiquinoline with a m.p. of 220°, representing 34.2% of the theoretical yield. The ether solution, which contained tolidine and the hexamethylbiquinoline dissolved in it, was processed with phthalic anhydride for one hour at room temperature. Then the ether was driven off, and the residue was treated with a 10% sodium hydroxide solution until all the tolidinephthalic acid had dissolved. The solution was decanted from the tarry residue, which dissolved freely in acidulated water. The action of alkali yielded 3.0 g of hexamethylbiquinoline with a m.p. of 193-195°, representing 13.1% of the theoretical

yield, the melting point rising to 220° after washing with alcohol. The overall yield of the hexamethylbiquinoline was 51.3% of the theoretical.

Synthesis of substantive biquinophthalonic dyes. We synthesized the biquinophthalones from the intermediates and sulfonated them in the usual manner, by the method described by A.E.Porai-Koshits and Kulikov [1]. The yields of the biquinophthalones were as follows: 75% of the theoretical from the benzidine intermediate; 69% from the dianisidine one; and 83% from the tolidine one.

Biquinophthalone from tetramethylbiquinoline: 0.2668 g substance: 12 ml N_2 (21.5°, 754 mm). Found %: N 5.03. $C_{38}H_{24}N_2O_4$. Computed %: N 5.00.

Biquinophthalone from dimethyldimethoxybiquinoline: 0.2274 g substance: 9 ml N_2 (19°, 761 mm). Found %: N 4.52. $C_{40}H_{28}N_2O_6$. Computed %: N 4.43.

Biquinophthalone from hexamethylbiquinoline: 0.2612 g substance: 10.2 ml N_2 (20.3°, 760 mm). Found %: N 4.44. $C_{40}H_{28}N_2O_4$. Computed %: N 4.67.

The biquinophthalones are dark-brown powders that do not fuse below 360°, but sublime partially. The biquinophthalones are sulfonated with a yield that is 95% of the theoretical. If the product with a m.p. of 193° secured from the ether extract is used to prepare a biquinophthalone from hexamethylbiquinoline, the yield of the biquinophthalone drops to 74% of the theoretical, but the resulting dye has the same properties as the dye synthesized from the hexamethylbiquinoline that has a m.p. of 225°.

SUMMARY

1. In synthesizing quinoline bases from aromatic diamines of the diphenyl series a difference is observed between the Beyer and Döbner-Miller reactions, the yields of the quinoline bases being much lower in the Döbner-Miller reaction.

2. The following crystalline products have been synthesized from diamines of the diphenyl series by the Beyer reaction: 2,2',4,4'-tetramethylbiquinoline, with a yield of 31% of the theoretical from benzidine; 2,2',4,4'-tetramethyl-8,8'-dimethoxybiquinoline, with a yield of 18%, from dianisidine; and 2,2'4,4,-8,8'-hexamethylbiquinoline, with a yield of 51%, from tolidine, these yields being, as far as we know, unprecedented in the Beyer reaction. The first of these products has been described in the literature, while the other two have been synthesized for the first time.

3. These intermediates have been used to synthesize biquinophthalonic dyes that are substantive. All three of these dyes have been synthesized for the first time.

4. Increasing the number of methyl groups or introducing methoxy groups into the aromatic rings of biquinophthalonic dyes deepens their color.

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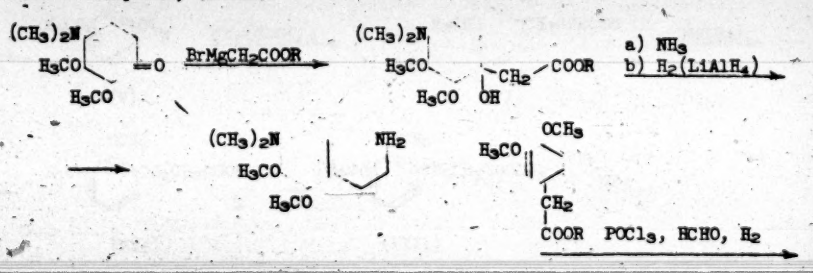
* See C.B.Translation a-85. ** See C.B.Translation 491. *** See C.B.Translation p. 493.

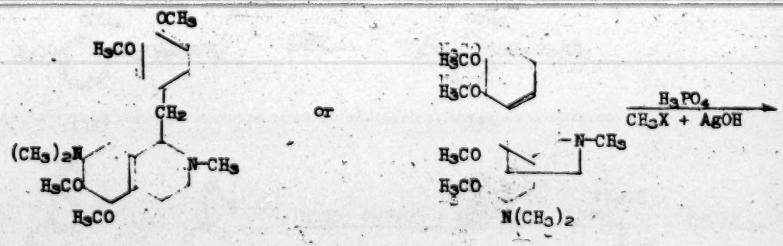
RESEARCH ON ISOQUINOLINE COMPOUNDS

III. SYNTHESIS OF N-METHYL-1-(3',4'-DIMETHOXYBENZYL-5,6-DIMETHOXY-1,2,3,4-TETRAHYDROISOQUINOLINE

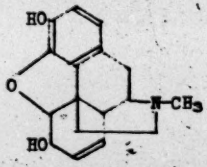
R. S. Livshits, M. S. Bainova, G. I. Bazilevskaya, E. I. Genkin, N. A. Preobrashensky and students Yu. M. Rozanova and Z. A. Baranova

In our previous report [1] we described the synthesis of N-Methyl-1-(4'-methoxybenzyl)-6-methoxy-1,2,3,4-tetrahydroisoquinoline methiodide, which contains a group resembling the structure of the alkaloid morphine. Pursuing our research on the syntheses of compounds whose structure resembles that of morphine, we have effected the synthesis of N-methyl-1-(3',4'-dimethoxybenzyl)-5,6-dimethoxy-1,2,3,4-tetrahydroisoquinoline (XXI) described in the present paper, which has the pattern of N-methyl-1-(3',4'-dimethoxybenzyl)-5,6-dimethoxy-7-dimethylamino-1,2,3,4,5,6,7,8-octahydroisoquinoline (XXII) – the principal intermediate in the synthesis of morphine, (XXIII):





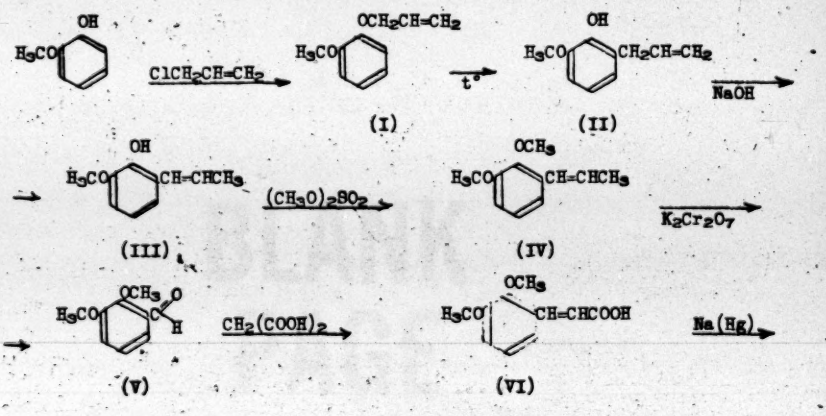
(XXII)



(XXIII)

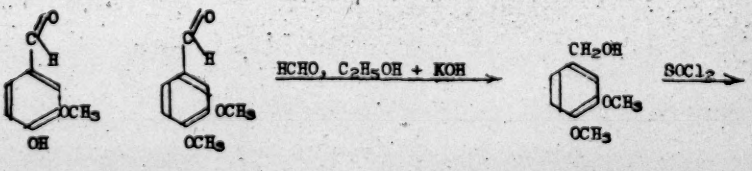
N-Methyl-1-(3',4'-dimethoxybenzyl)-5,6-dimethoxy-1,2,3,4-tetrahydroisoquinoline (XXI) was synthesized as follows:

A

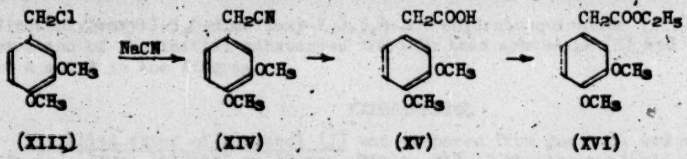


(I) (II) (III) (IV) (V) (VI) (VII) (VIII) (IX) (X)

B.

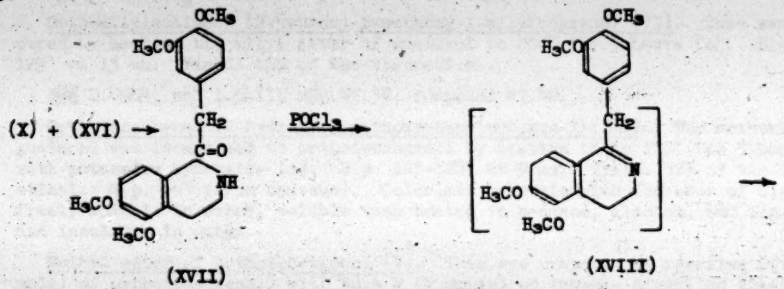


(XI) (XII)

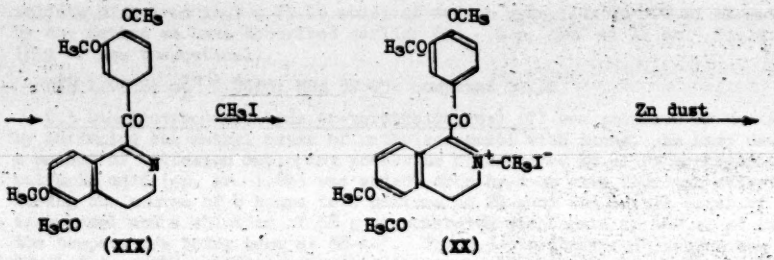


(XIII) (XIV) (XV) (XVI)

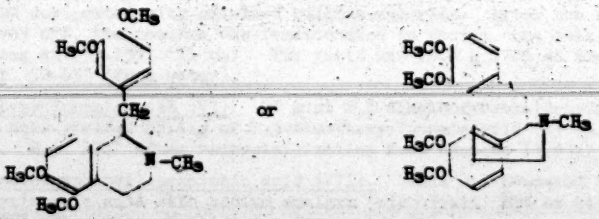
c.



(XVII) (XVIII)



(XIX) (XX)



(XXI)

Condensing β-(2,3-dimethoxyphenyl)-ethylamine (X) with the ethyl ester of 3,4-dimethoxyphenylacetic acid (XVI) yielded the corresponding amide (XVII). Heating the latter with phosphorus oxychloride converted it into 3',4'-dimethoxyphenyl-5,6-dimethoxy,3,4-dihydroisoquinolyl-(1) ketone (XIX), rather than into 1-(3',4'-dimethoxybenzyl)-5,6-dimethoxy-3,4-dihydroisoquinoline (XVIII). We have commented on transformations of this type in our preceding paper [1]. The methiodide of the ketone (XX) was reduced by zinc dust to N-methyl-1-(3',4'-

dimethoxybenzyl)-5,6-dimethoxy-1,2,3,4-tetrahydroisoquinoline (XXI). The preparation of the initial substances used in this synthesis (X) and (XVI) is given at A and B in the diagram.

EXPERIMENTAL

The allyl ester of guaiacol (I) was prepared from guaiacol and allyl chloride [2]. B.p. 111-113° at 13 mm. Yield: 74% of the theoretical.

d_{20}^{20} 1.0592; n_D^{20} 1.5362; MR_D 48.35 [3]; computed 47.6.

Orthoallylguaiacol (2-hydroxy-3-methoxy-1-allylbenzene) (II). This was prepared by heating the allyl ester of guaiacol to 230° for 3 hours [4]. B.p. 124-125° at 15 mm. Yield: 65% of the theoretical.

d_{20}^{20} 1.0904; n_D^{20} 1.5411; MR_D 47.32; computed 47.48.

Orthoisoeugenol (2-hydroxy-3-methoxyphenylpropene-1) (III). The orthoallyl guaiacol was isomerized to orthoisoeugenol by heating it to 170° for 5 hours with potassium hydroxide [2]. B.p. 125-128° at 9 mm. Yield: 52% of the theoretical. M.p. 66° (from benzene). Colorless crystals with the odor of cloves, freely soluble in ether, soluble when heated in benzene, alcohol, and ligroin, and insoluble in water.

Methyl ester of orthoisoeugenol (V). This was prepared by reacting 25 g (1 mole) of orthoisoeugenol with 38.4 g (2 moles) of freshly distilled dimethyl sulfate dissolved in 7 g (1.16 mole) of sodium hydroxide in 100 ml of methanol, by the method we have described earlier [1]. B.p. 128° at 11 mm. Yield: 24 g (89% of the theoretical).

d_{20}^{20} 1.0372; n_D^{20} 1.5535; MR_D 52.05; computed 52.22.

2,3-Dimethoxybenzaldehyde (o-veratraldehyde) (V) was prepared by Mauthner [2] by oxidizing the methyl ester of orthoisoeugenol with ozone. We have developed a method of oxidation employing potassium dichromate: 45 ml of concentrated sulfuric acid (sp. gr. 1.84) was added, drop-by-drop with thorough stirring, during the course of 8 hours to a mixture of 25 g of the methyl ester of orthoisoeugenol and a solution of 58 g of potassium dichromate in 480 ml of water, the temperature being kept at 38-40°. The 2,3-dimethoxybenzaldehyde was extracted from the reaction mixture with ether. The ether extract was washed with water and desiccated with calcined calcium chloride. After the solvent had been driven off, the residue was fractionated in vacuum, the bulk of the product boiling at 133-135° (11 mm). The yield was 16.8 g (70% of the theoretical). M.p. 52-63° (from water).

2,3-Dimethoxycinnamic acid (VI). 20 g of 2,3-dimethoxybenzaldehyde and 30 g of malonic acid yielded 23.4 g of 2,3-dimethoxycinnamic acid (83.6% of the theoretical). M.p. 177° after recrystallization from benzene [1,5].

β-(2,3-Dimethoxyphenyl)-propionic acid (VII). This was prepared by reducing 2,3-dimethoxycinnamic acid with sodium amalgam [1]. Yield: 85% of the theoretical. M.p. 68° after recrystallization from water [5].

Methyl ester of β-(2,3-dimethoxyphenyl)-propionic acid (VIII). 20 g of β-(2,3-dimethoxyphenyl)-propionic acid was heated with 200 ml of methanol and 10 ml of sulfuric acid (sp. gr. 1.84) to the boiling point of the solution for 8 hours. The ether was eliminated in the usual manner. B.p. 154-155° at 9 mm. Yield: 19.2 g (90% of the theoretical). A colorless liquid, soluble in organic solvents but insoluble in water.

d_{20}^{20} 1.127; n_D^{20} 1.5130; MR_D 59.73; computed 58.95.

2.654 mg substance: 6.245 mg CO_2; 1.730 mg H_2O. 2.878 mg substance: 6.780 mg CO_2; 1.860 mg H_2O. Found %: C 64.21, 64.29; H 7.29, 7.23. $C_{12}H_{16}O_4$. Computed %: C 64.25; H 7.19.

β-(2,3-Dimethoxyphenyl)-propionamide (IX). 15 g of the methyl ester of β-(2,3-dimethoxyphenyl)-propionic acid was shaken together with 150 ml of aqueous ammonia, saturated in the cold, for 10-12 hours until the oil vanished. Driving off the excess ammonia in vacuum yielded a crystalline precipitate of the amide. Yield: 12 g (86% of the theoretical). M.p. 99-100° after recrystallization from benzene [5].

β-(2,3-Dimethoxyphenyl)-ethylamine (X). A solution of potassium hypobromite, prepared with 16 g of bromine and 160 ml of 25% potassium hydroxide, was added to a suspension of 10 g of β-(2,3-dimethoxyphenyl)-propionamide in 130 ml of water. After the amide had been dissolved by shaking the flask, the solution was slowly heated to 60° over a water bath and kept at 60-65° for 2 hours. A layer of oil – the amine – separated out in the course of the reaction. The amine was extracted with chloroform and distilled in vacuum after it had been desiccated and the solvent had been driven off. B.p. 134-135° at 9 mm. Yield: 6.2 g (72.5% of the theoretical).

3,4-Dimethoxybenzaldehyde (paraveratraldehyde) (XI), was prepared by methylating vanillin with dimethyl sulfate [6]. The yield was 90% of the theoretical.

3,4-Dimethoxybenzyl alcohol (veratryl alcohol) (XII). 60 ml of a 50% solution of potassium hydroxide was added to 30 g of 3,4-dimethoxybenzaldehyde dissolved in 75 ml of 98% alcohol and 45 ml of 40% formalin at such a rate as to keep the temperature from rising above 40°. Then the temperature was slowly raised to 70°, stirring being continued for 40 minutes and then for another 20 minutes while the reaction mass boiled. After the mass had cooled, the alcohol was driven off in vacuum, and the resulting oil was extracted with ether. The ether extract was shaken up with sodium bisulfite and desiccated with calcined potash. B.p. 159-160° at 10 mm. The yield was 28.8 g (96% of the theoretical, [7]).

3,4-Dimethoxybenzyl chloride (XIII). This was prepared from 3,4-dimethoxybenzyl alcohol, with a yield that was 90% of the theoretical, by reacting it with thionyl chloride. M.p. 51° after recrystallization from alcohol [8].

3,4-Dimethoxybenzyl cyanide (XIV). This was prepared by reacting a benzene solution of 3,4-dimethoxybenzyl chloride with an aqueous solution of sodium cyanide. B.p. 168-170° at 9 mm. Yield: 68% of the theoretical. M.p. 68° after recrystallization from alcohol [8].

3,4-Dimethoxyphenylacetic acid (XV) was prepared by saponifying 3,4-dimethoxybenzyl cyanide, the yield being 87% of the theoretical. M.p. of the anhydrous acid 98-99°.

Ethyl ester of 3,4-dimethoxyphenylacetic acid (XVI). This was prepared by the usual method of esterification [8]. B.p. 159-160° at 5 mm. Yield: 85% of the theoretical.

β-(2,3-Dimethoxyphenyl)-ethyl-3',4'-dimethoxyphenylacetamide (XVII). 3 g (1 mole) of β-(2,3-dimethoxyphenyl)-ethylamine, 3.75 g of the ethyl ester of 3,4-dimethoxyphenylacetic acid, and a few drops of pyridine were heated to 180° for 3 hours over an oil bath. The reaction mass crystallized slowly in the cold and somewhat more rapidly when seeded. The crystalline precipitate was suction filtered and washed with ligroin. The yield was 3.7 g (62.3% of the theoretical). M.p. 89° after recrystallization from petroleum ether. Colorless crystals, soluble in alcohol, ether, and chloroform, insoluble in ligroin or water.

2.730 mg substance: 6.710 mg CO_2; 1.710 mg H_2O. 2.840 mg substance: 6.970 mg CO_2; 1.810 mg H_2O. 5.168 mg substance: 0.188 ml N_2 (20°, 746 mm). Found %: C 67.07, 66.97; H 7.01, 7.13; N 4.02. $C_{20}H_{25}O_5N$. Computed %: C 66.81; H 7.01; N 3.89.

3',4'-Dimethoxyphenyl-5,6-dimethoxy-3,4-dihydroisoquinolyl-(1) ketone (XIX). 2 g of β-(3,4-dimethoxyphenyl)-ethyl-3',4'-dimethoxyphenylacetamide was heated with 12 ml of phosphorus oxychloride for 2 hours over a boiling water bath. The base was recovered by the method we have described earlier [1]. Driving off the benzene in vacuum left behind a thick oil, which slowly crystallized in a vacuum desiccator. The yield was 1.3 g (65.7% of the theoretical). The crude base was triturated repeatedly with small batches of ether and then crystallized from alcohol. M.p. 119.5°. Colorless crystals, soluble in benzene, chloroform, and hot alcohol, sparingly soluble in ether, and insoluble in water.

2.805 mg substance: 6.935 mg CO_2; 1.535 mg H_2O. 2.717 mg substance: 6.733 mg CO_2; 1.482 mg H_2O. 5.385 mg substance: 0.205 ml N_2 (20°, 746 mm). Found %: C 67.47, 67.63; H 6.12, 6.10; N 4.19. $C_{20}H_{21}O_5N$. Computed %: C 67.57; H 5.96; N 4.10.

Methiodide of 3',4'-dimethoxyphenyl-5,6-dimethoxy-3,4-dihydroisoquinolyl-(1) ketone (XX). 1.3 g of the ketone was heated to a gentle boil with 15 ml of methyl iodide for 6 hours. After the mixture cooled, the precipitated methiodide was suction-filtered and washed repeatedly with anhydrous ether. The yield was 1.5 g (81.6% of the theoretical). M.p. 178-179° after crystallization from alcohol. Yellow crystals, soluble when heated in alcohol or water, sparingly soluble in these solvents in the cold.

2.563 mg substance: 4.763 mg CO_2; 1.102 mg H_2O. 2.845 mg substance: 5.300 mg CO_2; 1.250 mg H_2O. 6.789 mg substance: 0.192 ml N_2 (25°, 745.5 mm). Found %: C 50.71, 50.84; H 4.81, 4.92; N 3.03. $C_{21}H_{24}O_5NI$. Computed % C C 50.69; H 4.87; N 2.81.

N-Methyl-1-(3',4'-dimethoxybenzyl)-5,6-dimethoxy-1,2,3,4-tetrahydroisoquinoline (XXI). 1 g of the methiodide of 3',4'-dimethoxyphenyl-5,6-dimethoxy-3,4-dihydroisoquinolyl-(1) ketone was reduced with zinc dust by the method we have described previously [1]. Driving off the ether in vacuum left behind a solid residue. The yield was 0.5 g (69.6% of the theoretical). M.p. 76-77° after recrystallization from ligroin. Minute crystals, soluble in alcohol, benzene, chloroform, and ether, insoluble in water.

1.931 mg substance: 5.00 mg CO_2; 1.300 mg H_2O. 8.087 mg substance: 0.293 ml N_2 (17°, 730 mm). 3.292 mg substance: 0.116 ml N_2 (19°, 747 mm). Found %: C 70.61; H 7.53; N 3.98, 4.03. $C_{21}H_{27}O_4N$. Computed %: C 70.54; H 7.62; N 3.92.

The hydrochloride was prepared by reacting ether solutions of the base with hydrogen chloride, the oil that separated out crystallizing upon standing. The ether solution was decanted, and the precipitate was stirred two or three times with absolute ether and dried in a vacuum desiccator. M.p. 139-141°. Soluble in alcohol and water, insoluble in ether.

4.386 mg substance: 0.143 ml N_2 (19.5°, 746 mm). 2.800 mg substance: 0.091 ml N_2 (18°, 748 mm). Found %: N 3.67, 3.77. $C_{21}H_{28}O_4NCl$. Computed %: N 3.55.

SUMMARY

N-Methyl-1-(3',4'-dimethoxybenzyl)-5,6 dimethoxy-1,2,3,4-tetrahydroisoquinoline has been synthesized; it has the pattern of N-methyl-1-(3',4'-dimethoxybenzyl)-5,6-dimethoxy-7-dimethylamino-1,2,3,4,5,6,7,8-octahydroisoquinoline –

the principal intermediate in the synthesis of morphine.

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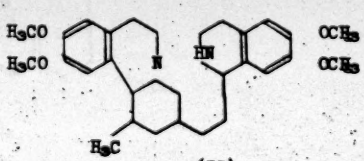
RESEARCHES ON ISOQUINOLINE COMPOUNDS

IV. SYNTHESIS OF 1-[β-(3 -PYRIDYL)-ETHYL]-6,7-DIMETHOXY-1,2,3,4-TETRAHYDROISOQUINOLINE

R. S. Livshits, R. P. Evstigneeva, M. S. Rainova, and N. A. Preobrazhensky

Numerous researches on the synthesis of substitutes for complicated physiologically active natural compounds have shown it is often sufficient to have certain groups and a similar arrangement of the atoms present in the molecule to achieve the same therapeutic effect. We undertook an investigation along these lines with a view to synthesizing the analog (I) of the alkaloid emetine (II),* which differs from the natural substance in not having a methyl group in the piperidine ring and having one of the isoquinoline rings open.

(I)



(II)

Brindley and Pyeman formula

In this report we describe the first half of our research: the synthesis of 1-[β-(3'-pyridyl)-ethyl]-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (III).

This compound was synthesized as follows:

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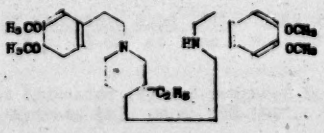
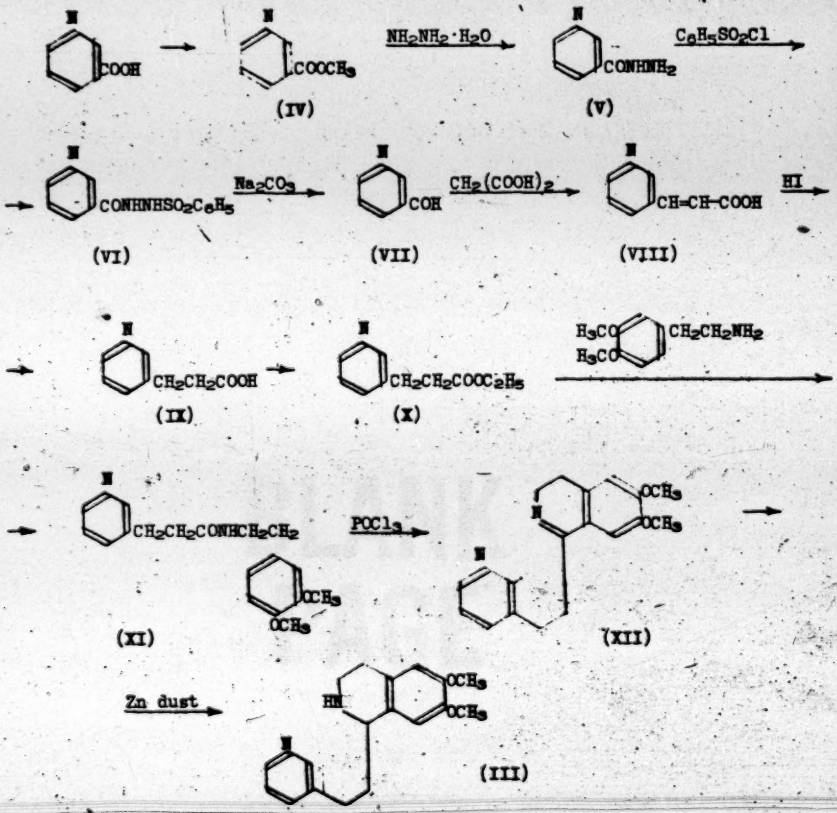
*While the present paper was in the hands of the editor, the authors of the paper, in association with L. I. Zakharkin, completed their research on the synthesis of emetine, determining its structure as 4', 5'-dimethoxy-6-ethyl-7-(1" -methyl-6", 7" -dimethoxy-1", 2", 3", 4" -tetrahydroisoquinolyl)-3,4,5,6,7,8,9,10-octahydro-1,2 : 1',2'-benzoquinoline, represented by the formula:





We prepared β-(3-pyridyl)-acrylic acid (VIII) on the whole by the method described in the literature. It was converted into β-(3-pyridyl)-propionic acid (IX) by reducing it with hydriodic acid. Condensation of the ethyl ester of the reduced acid (X) with β-(3,4-dimethoxyphenyl)-ethylamine yielded the corresponding amide (XI). Reaction with phosphorus oxychloride converted the amide into 1-[β-(3'-pyridyl)-ethyl]-6,7-dimethoxy-3,4-dihydrotetraisoquinoline (XII), which was reduced with zinc dust to 1-[β-(3'-pyridyl)-ethyl]-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (III).

EXPERIMENTAL

Methyl ester of nicotinic acid (IV). This was prepared by the usual method of esterification. B.p. 89-90° at 7 mm. M.p. 38°. Yield: 80% of the theoretical [1].

Nicotinic acid hydrazide (V) was prepared from the methyl ester of nicotinic acid and hydrazine hydrate [2]. M.p. 158-159°. Yield: 98-99% of the theoretical.

The benzenesulfohydrazide of nicotinic acid (VI) was prepared by condensing nicotinic acid hydrazide with benzene sulfochloride at 0°, the yield being 96.5% of the theoretical. M.p. 182-183°, and 185-186° after recrystallization from alcohol [3].

Nicotinaldehyde (VII) was prepared by heating the benzenesulfohydrazide of nicotinic acid in ethylene glycol to 160° for 2 minutes with sodium carbonate. [3]. The yield was 28-30% of the theoretical. M.p. 85-90° at 12 mm.

β-(3-Pyridyl)-acrylic acid (VIII) was prepared by condensing nicotinaldehyde with malonic acid [3]. M.p. 230-232°, and 232-233° after recrystallization from alcohol. Yield: 67-70% of the theoretical.

β-(3-Pyridyl)-propionic acid (homohomonicotinic acid) (IX). 8 g of β-(3-pyridyl)-acrylic acid, 40 ml of glacial acetic acid, 80 ml of hydriodic acid (sp. gr. 1.71), and 3 g of red phosphorus were heated together over an oil bath for 14-15 hours, to a gentle boil, with constant stirring. After the reaction mass had cooled, it was diluted with 50 ml of water. After the excess phosphorus had been filtered out, the filtrate was evaporated to dryness in vacuum. The crystalline hydriodide of β-(3-pyridyl)-propionic acid was washed repeatedly with anhydrous acetone. The yield was 13.5 g (90% of the theoretical). It crystallized as colorless lamellae, which were freely soluble in water and boiling alcohol. M.p. 163-164°.

6.875 mg substance: 0.314 ml N_2 (22°, 740 mm). 5.135 mg substance: 0.227 ml N_2 (17°, 736 mm). Found %: N 5.04, 5.04. $C_8H_{10}O_2NI$. Computed %: N 5.02.

A solution of 8 g of sodium diphosphate in 12 ml of water was added to a hot solution of 4 g of the hydriodide of β-(3-pyridyl)-propionic acid in 8 ml of water, and the resultant solution was evaporated in vacuum to dryness. The dry residue was boiled with butyl alcohol several times. When the filtrate was chilled to 0°, a finely crystalline precipitate of β-(3-pyridyl)-propionic acid settled out. The yield was 2.1 g (99% of the theoretical). It crystallized from alcohol as minute, colorless, rhombic crystals. M.p. 157-158°. Soluble in water and boiling alcohol, insoluble in ether, benzene, or ligroin.

3.000 mg substance: 6.990 mg CO_2; 1.670 mg H_2O. 3.545 mg substance: 8.295 mg CO_2; 1.875 mg H_2O. 3.146 mg substance: 0.253 ml N_2 (16°, 738 mm). 2.887 mg substance: 0.230 ml N_2 (15°, 739 mm). Found %: C 63.54; 63.80; H 6.22, 5.92; N 9.23, 9.18. $C_8H_9O_2N$. Computed %: C 63.55; H 6.00; N 9.27.

Ethyl ester of β-(3-pyridyl)-propionic acid (X). 8 g of the crude hydriodide of β-(3-pyridyl)-propionic acid was heated with 80 ml of absolute ethyl alcohol to a gentle boil for 8 hours while anhydrous hydrogen chloride was passed through the mixture. Then the excess alcohol was driven off in vacuum, and the residue was poured into cold water. The solution was decolorized by adding a few drops of sodium bisulfite, after which it was processed with sodium carbonate until its reaction was alkaline. The ethyl ester of β-(3-pyridyl)-propionic acid was repeatedly extracted with ether. After the solvent had been driven off, the residue was distilled in vacuum. B.p. 129-130° at 7 mm. Yield: 3.9 g (75.7% of the theoretical).

A colorless liquid, soluble in organic solvents and in water.

n_D^{20} 1.4983; d_{20}^{20} 1.071; MR_D 49.13; computed 49.57.

2.910 mg substance: 7.150 mg CO_2; 1.965 mg H_2O. 3.070 mg substance: 7.510 mg CO_2; 2.07 mg H_2O. 3.343 mg substance: 0.240 ml N_2 (19.5°, 744 mm). 2.944 mg substance: 0.216 ml N_2 (19.5°, 744 mm). Found %: C 67.0, 66.71. H 7.55, 7.54; N 8.05, 8.21. $C_{10}H_{13}O_2N$. Computed %: C 67.0; H 7.31; N 7.81.

Treating an ether solution of the ethyl ester of β-(3-pyridyl)-propionic acid with ether that had been saturated with hydrogen chloride yielded the crystalline hydrochloride. It was purified by precipitating it from an alcoholic solution with ether. Colorless crystals, soluble in water and in alcohol, insoluble in ether. M.p. 95-96°. Highly hygroscopic.

4.767 mg substance: 0.270 ml N_2 (20°, 746.5 mm). 3.461 mg substance: 0.210 ml N_2 (17°, 722 mm). Found %: N 6.48, 6.40. $C_{10}H_{14}O_2NCl$. Computed %: N 6.49.

The picrate was prepared by reacting ether solutions of the ethyl ester of β-(3-pyridyl)-propionic acid and picric acid together. It crystallized from alcohol as minute yellow parellelograms. M.p. 81-82°. Soluble in water and in hot alcohol, insoluble in ether.

4.246 mg substance: 0.517 ml N_2 (20.5°, 743 mm). 4.051 mg substance: 0.494 ml N_2 (21°, 743 mm). Found %: N 13.60, 13.57. $C_{16}H_{16}O_8N_4$. Computed %: N 13.68.

β-(3,4-Dimethoxyphenyl)-ethyl-β-(3'-pyridyl)-propionamide (XI). 3 g of the ethyl ester of β-(3'-pyridyl) propionic acid, 3 g of β-(3,4-dimethoxyphenyl)-ethylamine [4], and a few drops of anhydrous pyridine were heated to 180° for 3 hours over an oil bath. The amide crystallized out after the reaction mass had stood for a long time (10-12 hours, the time being shortened when a seed crystal was used). It was suction-filtered out and washed repeatedly with anhydrous ligroin. The yield was 4.2 g (80.7% of the theoretical). It crystallized from water as colorless needles. M.p. 103°. Soluble in alcohol, benzene, chloroform, and ether, and when heated in water or petroleum ether; insoluble in ligroin.

2.748 mg substance: 0.217 ml N_2 (19°, 744 mm). 3.960 mg substance: 0.323 ml N_2 (20°, 727 mm). Found %: N 8.90, 9.09. $C_{18}H_{22}O_3N_2$. Computed %: N 8.91.

1-[β-(3'-Pyridyl)-ethyl]-6,7-dimethoxy-3,4-dihydroisoquinoline (XII). 2 g of β-(3,4-dimethoxyphenyl)-ethyl-β-(3'-pyridyl)-propionamide was heated with constant stirring over a boiling water bath with 12 ml of phosphorus oxychloride for 2.5 hours. The cooled reaction mass was poured over ice cautiously. The solution was decolorized in the cold with charcoal and treated with soda until its reaction was alkaline. The isoquinoline base was extracted with ether, and the ether extract was desiccated with calcined potash.

Driving off the solvent left behind a thick yellow mass, which crystallized when left to stand in a vacuum desiccator. The yield was 1.6 g (85% of the theoretical). It crystallized from petroleum ether as colorless polyhedra. M.p. 88-89°. Soluble in alcohol, benzene, chloroform, and ether; insoluble in water.

3.290 mg substance: 8.789 mg CO_2; 1.945 mg H_2O. 2.620 mg substance: 7.000 mg CO_2; 1.480 mg H_2O. 3.995 mg substance: 0.322 ml N_2 (17.5°, 754 mm). 4.290 mg substance: 0.354 ml N_2 (20.5°, 736 mm). Found %: C 72.72, 72.85; H 6.61, 6.31; N 9.26, 9.29. $C_{18}H_{20}O_2N_2$. Computed %: C 72.93; H 6.65; N 9.42.

The hydrochloride was prepared by treating an ether solution of the isoquinoline base with ether that had been saturated with hydrogen chloride. It crystallized from alcohol as colorless needles. M.p. 198-200°. Soluble in water and when heated in alcohol.

4.438 mg substance: 0.287 ml N_2 (21.5°, 732 mm). Found %: N 7.22. $C_{18}H_{20}O_2N_2 \cdot 2HCl$. Computed %: N 7.58.

1-[β-(3'-Pyridyl)-ethyl]-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (III). A mixture consisting of 1 g of 1-[β-(3'-pyridyl)-ethyl]-6,7-dimethoxy-3,4-dihydroisoquinoline, 30 ml of water, 4 g of zinc dust, and 0.1 g of copper sulfate was heated over a boiling water bath and constantly stirred while 3 ml of concentrated sulfuric acid was added during the course of an hour at such a rate as to prevent the excessive evolution of hydrogen. Then heating was continued for another 2 hours. The unreacted zinc was filtered out, and the cooled filtrate was treated with soda.

The precipitated zinc hydroxide was dissolved by adding ammonia, and the reduced isoquinoline base was extracted with ether. After it had been desiccated and the solvent had been driven off, there was left a noncrystallizing, thick, yellow oil. The yield was 0.7 g (70% of the theoretical).

The hydrochloride was prepared from an ether solution. It crystallized from alcohol as minute colorless crystals. M.p. 241-243°. Soluble in water and in hot alcohol.

3.205 mg substance: 6.795 mg CO_2; 1.815 mg H_2O. 2.975 mg substance: 6.330 mg CO_2; 1.665 mg H_2O. 4.382 mg substance: 0.298 ml N_2 (16°, 732 mm). 3.837 mg substance: 0.260 ml N_2 (16.5°, 739 mm). Found %: C 58.12, 58.02; H 6.33, 6.26; N 7.65, 7.58. $C_{18}H_{23}O_2N_2Cl$. Computed %: C 58.19; H 6.51; N 7.54.

SUMMARY

1-[β-(3'-Pyridyl)-ethyl]-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline has been synthesized via a number of intermediate products, many of which are not described in the literature. The preparation of this compound opens the way to the synthesis of analogs of the alkaloid emetine, resembling the latter in structure.

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*See C.B. Translation.